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# A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

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## SHORT SUMMARY

ON the basis of the model of the water molecule derived from spectral and x-ray data and a proposed internal structure for water, the following properties of water and ionic solutions have been deduced quantitatively in good agreement with experiment.

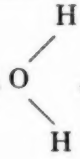
(1) The crystal structure of ice.
(2) The x-ray diffraction curve for water.
(3) The total energy of water and ice.
(4) The degree of hydration of positive and negative ions in water.
(5) The heats of solutions of ions.
(6) The mobility of hydrogen and hydroxyl ions in water.

And the following inferred in a qualitative way.

(7) The density and density changes of water.
(8) The explanation of the unique position of water among molecular liquids.
(9) The dielectric properties of water and ice.
(10) The viscosities of dilute ionic solutions.
(11) The viscosities of concentrated acids.

## FULL SUMMARY. PART I

### 1

A consideration of the spectroscopic molecular model of $H_2O$,  , of the crystal structure of ice, and of the density of water, leads to the proposing of an irregular four-coordinated structure for water. This structure is tested and found to account for the positions of the maxima of x-ray diffraction by water, and for the change in these positions with temperature, which are quite different from those of a simple liquid such as mercury. Three different intermolecular arrangements are postulated for water at different temperatures.

(1) Ice-tridymite-like (four-coordinated) at low temperatures below 4°C.

(2) Quartz-like (four-coordinated) between 4–200°C, roughly.

(3) Ammonia-like, close-packed, 200–340°C.

These forms are not distinct and pass continuously into each other. This hypothesis accounts for the abnormal changes of density of water. It is further tested by the behaviour of water under pressure, and by the Raman spectra of water at different temperatures.

### 2

The large dielectric constant of water and ice, and its variation with temperature and frequency is discussed, and it is concluded that it can be explained by existing theories based on molecular rotation, but only if by far the greater part of the water molecules are not free to respond by orientation to the external electric field. In the course of this discussion a new structure for ice

is proposed, based on electrostatic grounds and accounting for the position of the H atoms.

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The physical properties of water are compared with those of its neighbours in the periodic table, particularly with $NH_3$, HF, $H_2S$, and $CH_3OH$. This discussion brings out the fact that the unique position of water is due not only to its dipole character but even more to the geometrical structure of its molecule, which is the simplest one that can form extended four-coordinated networks.

It has been found possible to calculate on the basis of this model the total energy of ice and water, due mainly to the electrostatic potential of neighbouring molecules, and the agreement with experiment furnishes another proof of the correctness of the hypothesis.

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Turning now to ionic solutions, we discuss the nature of ionic hydration. A method of estimating the degree of hydration from the specific gravity of the solutions is developed, and the results compared with those calculated theoretically on the basis of the molecular model. It is concluded that all the strongly polarizing ions $H^+$, $Li^+$, $Na^+$, and all divalent and trivalent positive ions as well as $(OH)^-$ and $F^-$ are hydrated, while $(NH_4)^+$, $Rb^+$, $Cs^+$, and most negative ions are not. The degree of hydration depends mainly on the ionic radius and is the same in solutions as in crystals: e.g., $Be.4H_2O$, $Mg.6H_2O$.

Further it has been shown possible to calculate the total heat of solution of any atomic ion. This is to a first approximation of the form $a+bP$ where $P$ is the mutual potential of the ion and a water molecule depending on the radius and charge of the ion while $a$ and $b$ depend only on the ionic charge. This formula gives excellent agreement with experiment.

The effects of the ions on the water in which they are dissolved is discussed, and from a study of various properties, particularly viscosity, it is concluded that their effect is that of increasing or decreasing the intermolecular coherence and regularity. The concept of a structural temperature is introduced, which is increased by large and decreased by small ions. With respect to these properties, $H^+$ and $(OH)^-$ ions appear quite anomalous, and on this account, as well as for their mobility, require a new theory.

## PART II

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The $H^+$ ion must exist in solution as $(OH_3)^+$. But this makes the anomalous mobility of $H^+$ still more difficult to account for. A break with current theory is proposed. The hydrogen positive ion, effectively $(OH_3)^+$ moves through water under a potential gradient of 1 volt/cm at a rate $32.5\times10^{-4}$ cm/sec. at room temperature. The corresponding rate for $(OH)^-$ is $17.8\times10^{-4}$, and for all other ions much less (e.g., $K^+$, $(NH_4)^+$, $Cl^-$, $6.7\times10^{-4}$). This discrepancy is analysed and it is claimed that the excess velocities of these ions over $6.7\times10^{-4}$ cm/sec. must be due to a mechanism entirely different from bodily transport through the solution. It is suggested that this different mechanism is the transfer by a jump of one proton from one water molecule to another when favourable configurations are presented. Such an idea has also been proposed by Hückel but quite differently developed by him. This transfer is analysed quantum-mechanically with simple models, and it is shown that the result of the imposed e.m.f. will be to cause a bias in the transfers in favour of transfer down the field, and that the order of magnitude of this bias on the most reasonable assumptions as to distances and heights of potential barriers is just such as to account for the extra (abnormal) velocity of these ions in water. The hydrogen isotope $H^2$ will possess practically no extra (abnormal) velocity, and therefore have a mobility about 1/5 that of $H^1$. The explanation given automatically leaves unaffected the ordinary theory of the mobilities of *foreign* ions in water. The theory requires the degree of organization in the structure of water to be considerable, in complete agreement with the discussions of Part I.

### INTRODUCTION

### §1. The abnormal mobilities of $H^+$ and $(OH)^-$ in water

The present theories of ionic mobility are based on a picture of water as a homogeneous

fluid, of definite viscosity and dielectric constant varying with the temperature, and on a picture of ions as spherical charged particles subject to resisting forces proportional to their velocity. This accounts satisfactorily for the mobilities of large ions, $K^+$, $Cl^-$, etc., and also for the slower mobility of small ions on the hypothesis of a rather indefinite amount of hydration. More exact fit can be obtained for concentrated solutions by taking into account the mutual electrostatic interactions of the ions as in the Debye-Hückel-Onsager theory.

However, all such theories fail to account for the mobilities of the ions $H^+$ and $(OH)^-$ in water. The equivalent Stokes law radii for $H^+$ and $(OH)^-$ calculated from their mobilities* are $2.6\times10^{-9}$ cm and $4.8\times10^{-9}$ cm, quite impossibly small on physical grounds (and neither hydration nor ionic interaction can do anything but reduce mobility). These abnormal mobilities of the $H^+$ and $(OH)^-$ ions are confined to water and closely related solvents, e.g., methyl alcohol, and it is clear that to explain them it is necessary to examine more closely the molecular structure of water in order to show where the hypothesis of the simple viscous dielectric fluid fails to give an adequate account of experimental facts. A study of the anomalous mobility of the $H^+$ ion which was our original theme has thus turned itself into a general attack on the nature of water, expounded in Part I. We return to the original theme in Part II.

## Part I. The Structure of Water and Ionic Aqueous Solutions

### §2. Nature of the water molecule

Pure water, apart from a slight natural ionisation, consists of molecules of $H_2O$. There is no reason to assume that these molecules, except for small mutual deformations, differ from the $H_2O$ molecules in steam. This is supported by the evidence of Raman and infrared absorption spectra of water. The $H_2O$ molecule in steam consists according to the last results of Mecke[1] from band spectra, of a V-shaped arrangement of the nuclei, the OH distances being 0.96A and the HÔH angle 103°–106°, very nearly the tetrahedral angle 109°.†

It is more difficult to picture the electronic distribution. If it were simply spherical and centred on the O nucleus the molecular dipole moment would be $5.6\times10^{-18}$ e.s.u. instead of $1.87\times10^{-18}$ as observed. There must, therefore, be a considerable screening effect by a concentration of negative charge around the protons. (See below, p. 529.) The wave mechanical theory of the water molecule gives some qualitative information on this point. According to Mulliken[2] the 10 electronic wave functions of the water molecule can be designated as

$$(1s)^2[2s_1]^2[2p_z]^2[2p_y]^2[2p_x]^2$$

where $x$, $y$, and $z$ are orientated as in Fig. 1; of these $[2s_1]^2[2p_z]^2[2p_y]^2$ are responsible for the binding of the protons and combined give an electron density surrounding the protonic positions, while $[2p_x]^2$ is not a binding wave function and gives a concentration of negative electricity

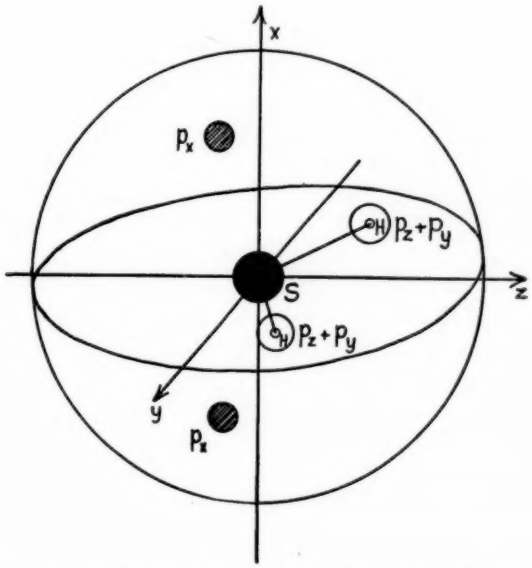


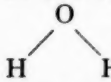

Fig. 1. The electron distribution in the water molecule.

* By direct calculation from $6\pi a\zeta v = F$ ($a$ radius, $\zeta$ viscosity), where $v=32.5$, 17.8, $\times10^{-4}$ cm/sec. for a field $F$ of 1 volt/cm.

[1] Mecke and Baumann, Phys. Zeits. **33**, 833 (1932).

† These results cannot be taken as exact since no fine structure analysis of the rotation spectra of an asymmetrical top has yet been completed. But most spectroscopists would agree that the molecule forms an isosceles triangle, that the vertex angle is between 90° and 120°, and that the OH distance lies between 0.9 and 1.1A.

[2] Mulliken, Phys. Rev. **41**, 756 (1932).

in two regions at right angles to the plane of  . The net electronic density distribution will therefore resemble a tetrahedron with two corners of positive and two of negative charge.

The "radius" of the water molecule is more easily fixed. The nearest approach of water molecules in ice[3] is 2.76A, and very similar figures follow from the most reliable measurements of water of crystallisation.[4] This would make the radius of the water molecule 1.38A, slightly larger than that of the isoelectronic $O^{--}$ (1.35) and $F^-$ (1.33), $(OH)^-$ (1.33) ions, but considerably smaller than that of A (1.9), $CH_4$ (2.08) or $NH_3$ (1.80) also measured in the solid state.

### §3. The arrangement of water molecules in water

If we attempt to account for the structure of water on the basis of such a molecule and a knowledge of the structure of simple monatomic liquids such as mercury, we are faced at the outset by the difficulty of accounting for the density. A simple disordered close packed assembly of water molecules of radius 1.4A would have a density of 1.84; or conversely, for a density of 1.00 the equivalent radius would be 1.72A. We have therefore the choice of assuming either that water is a simple close packed liquid in which the effective molecular radius has changed from 1.4A in the solid to 1.72A in the liquid, or that the radius is still approximately 1.4A but that the mutual arrangements of the molecules are far from that of a simple liquid. Both all the well-known abnormal properties of water and the extremely asymmetrical and electropolar properties of the $H_2O$ molecule would lead us to the latter alternative, but here luckily there exists independent evidence from x-ray diffraction as to the internal structure of water.

The best results on the x-ray diffraction of water corrected for absorption, Compton effect, incoherent scattering, etc., are furnished by the independent researches of Meyer,[5] Steward[6] and Amaldi,[7] all of whom are in almost perfect agreement. The observed diffraction curve of water is shown in Fig. 2, experimental curve (2). This curve shows immediately by contrast with that of mercury, which is similar to curve (1) Fig. 2 the theoretical curve for random close packing, that the association of molecules in water is different from that of a simple liquid, for instead of the sequence of maxima in the theoretical sequence at equivalent spacings of 2.6, 1.65, 1.1A we have a very strong maximum at 3.27A followed by very much weaker ones at 2.3A and 1.4A. It is more difficult to find what is the variation from the simple liquid arrangement. The best method is to build up models of the distribution functions of the molecules (i.e., the function $g(r)$ giving the probability of finding the centre of any molecule between distances $r$ and $r+dr$ from the centre of a given molecule) on different hypotheses, to construct from these, according to the formula[8]

$$I_\theta = \int_0^\infty 4\pi r^2 \{g(r) - \rho\} \frac{\sin sr}{sr} dr, \qquad (1)$$

where

$$s = (4\pi \sin \tfrac{1}{2}\theta)/\lambda, \qquad (2)$$

the theoretical x-ray diffraction, and to compare it with experiment. Various functions $g(r)$ are shown in Fig. 3, and the deduced x-ray scattering curves in Fig. 2 and Fig. 5.

Curve $a$ of Fig. 3 represents $g(r)$ for a simple close packed liquid arrangement, curve $b$ for an ice-like arrangement, and $c$ for one somewhat similar to quartz. It can be seen that only $b$ and $c$ give diffraction curves at all resembling the observed curve, with greater resemblance in the case of $c$.

The distribution $a$ is constructed for molecules of radius 1.4A. The distributions $b$ and $c$ are constructed on the basis of an $H_2O$ molecule of 1.4A radius, each of which is surrounded by four others in a more or less regular tetrahedron (Fig. 4). This is the arrangement found in ice and necessarily follows from the quasi-tetrahedral angle of the $H_2O$ molecule. The proton near the surface of one molecule lies opposite the empty

[3] Barnes, Proc. Roy. Soc. **A125**, 670 (1929).

[4] Cf. C. Beevers and H. Lipson, Zeits. f. Kryst. **82**, 297 (1932); **83**, 123 (1932).

[5] A. W. Meyer, Ann. d. Physik **5**, 701 (1930).

[6] Steward, Phys. Rev. **35**, 1426 (1930); **37**, 9 (1931).

[7] Amaldi, Phys. Zeits. **32**, 914 (1931).

[8] Debye and Menke, Phys. Zeits. **31**, 799 (1930); Prins, Zeits. f. Physik **56**, 617 (1929).

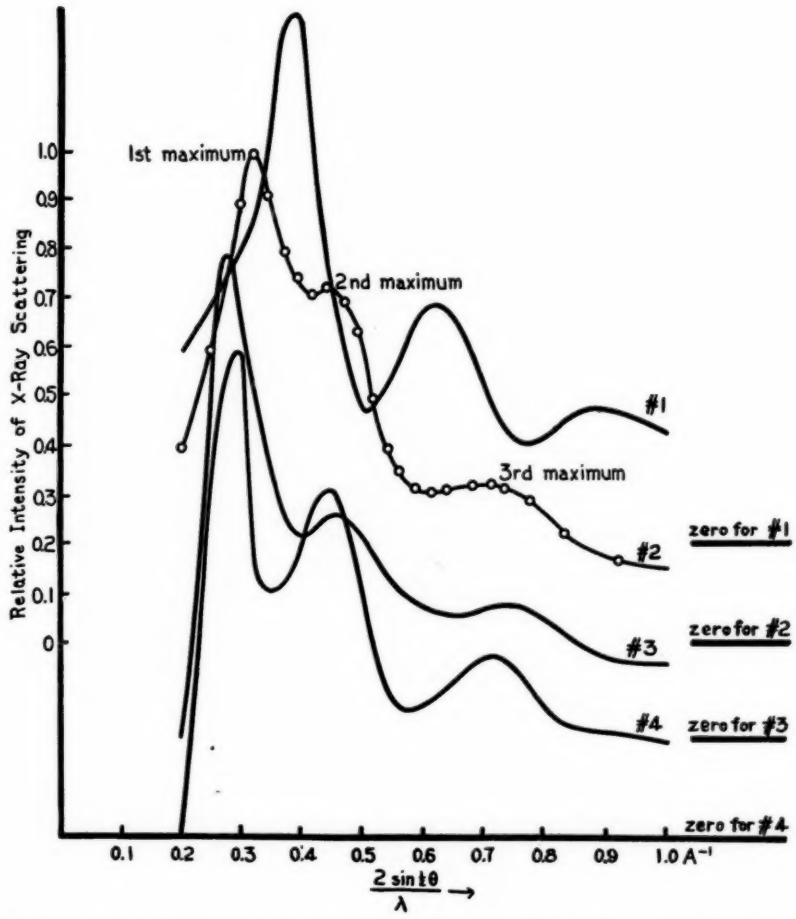



FIG. 2. X-ray scattering curves for water. Curve 1, theoretical curve for irregular close packing; curve 2, experimental curve; curve 3, theoretical curve for a quartz-like distribution; curve 4, theoretical curve for an ice-trydymite-like distribution.

place in a neighbouring molecule, that is a place where a proton would be in such a molecule as $CH_4$. These are just the positions of the concentration of negative elasticity due to the wave function $[2p_x]^2$, Fig. 1.

Such fourfold coordination of molecules is not, however, sufficient to fix the whole distribution. In the case of silica, $SiO_2$, where a similar fourfold coordination holds, there are three main crystalline forms, cristobalite, tridymite and quartz, besides the amorphous silica glass. Of these the tridymite structure corresponds to that of ordinary ice, and it would seem natural to imagine water as simply an irregular version of this (distribution *b*). It is difficult, however, in this case to account for the great diminution of volume on passing from ice to water. A regular crystalline arrangement might be expected to increase in volume on becoming irregular. This suggests the possibility that water does not correspond in the main to the ice-tridymite pattern, but to the quartz pattern. In such a pattern, while the intermolecular distance between nearest neighbours is the same at 2.8A, that between next nearest decreases to 4.2A from the 4.5A in the ice-tridymite pattern, leading to a 17 percent decrease of volume. Remembering that the density of ice is 0.91 which is therefore the density of the ice-tridymite structure, the density of the corresponding quartz pattern would be 1.08. Water might reasonably be expected to have a lower density due to irregularities. A closer examination of the theoretical curves enables these considerations to be pushed much

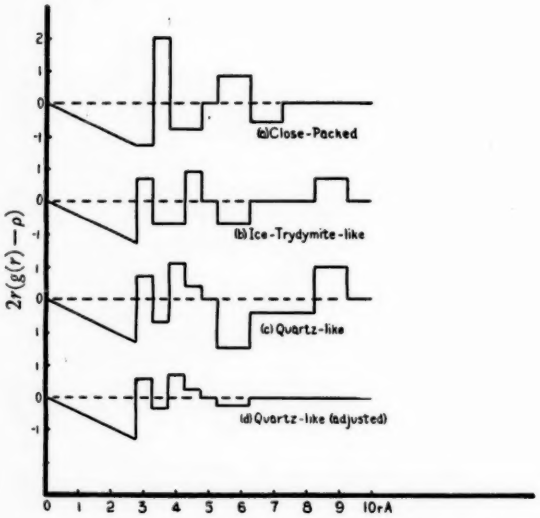



FIG. 3. The distribution function $g(r)$ for the neighbours around a water molecule (closest distance of approach 2.76A) for various types of arrangement.

further. The chief difference between curve 3 of Fig. 2 for the quartz-like distribution and the observed curve is that the main maxima of the former are at spacings 3.5 and 2.2 instead of 3.3 and 2.3, and that the intervening minimum at 2.5 is relatively much deeper—42 percent of the chief maximum instead of 72 percent. It is at once apparent that this may be due to a tendency towards a close packed water arrangement (curve 1) which has a maximum precisely in this region. It can be seen from the distribution curves for $g(r)$ that beyond $r=2.7$A the density of the quartz and close packed structures are out of step for the same radii and consequently the effect of adding distribution *a* to *b* is to smooth out differences from that of a uniform fluid or, physically speaking, to diminish the regularity of the packing particularly at greater distances than 4A from any molecule. A scattering curve constructed from such an altered distribution function (*d* of Fig. 3) is shown in curve 5 of Fig. 5. It shows an almost perfect fit with the experimental curve as far as the position of the maxima and minima, but it still differs in intensity, the second maximum being undoubtedly low compared with the first. The physical basis of the difference between the ideal quartz-like structure and the actual water structure is the temperature movement of the molecules. At higher temperatures this causes a breakdown of the quartz structure, leading more and more toward the close packed structure, and shows itself in the x-ray pattern as a shift of the first and second maxima in opposite directions towards the mean position of 2.7A, and of the wiping out of the minimum between them. Thus between 2° and 98° the main maximum moves from 3.27 to 3.1, while the second moves from 2.2 to 2.4 at 40° and afterwards disappears.

The inward movement of the main maximum gives rise to the appearance of a contraction on heating water which can now be seen to be

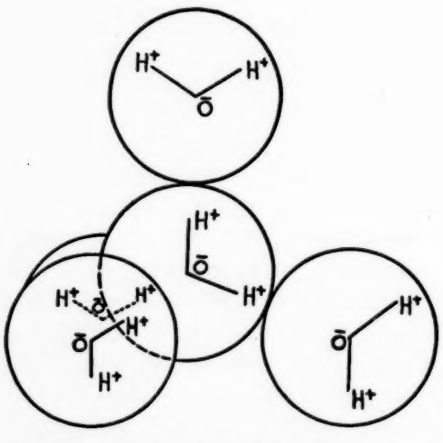



FIG. 4. Tetrahedral coordination of water molecules. The four molecules surrounding one water molecule are shown. Of these, two are in the plane of the paper, one above and one below it.

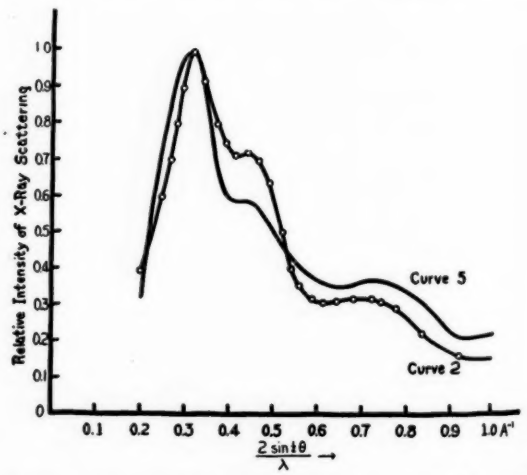



FIG. 5. X-ray scattering curves for water. Curve 2, experimental; curve 5, theoretical curve for quartz-like water modified by some close packing.

| | max. | min. | max. | min. | max. | min. |
|---|---|---|---|---|---|---|
| Observed | 3.27 | 2.37 | 2.27 | 1.60 | 1.45 | 1.1 |
| Calculated | 3.33 | 2.4 | 2.2 (inflection) | 1.55 | 1.40 | 1.1 |

spurious. At the lowest temperatures, 2°C, the deepening of the first minimum suggests a distribution in which the tridymite-ice-like arrangement is beginning to occur. This arrangement might be expected to be common in supercooled water, and its disappearance the reason for the anomalous contraction of water on heating above 0°C. But as these anomalous changes of volume are small compared with the ice-water change, we must not say more than that cold water is on the whole quartz-like with appreciable tridymite-ice-like tendencies.

We may therefore consider that there are three chief forms of arrangement of the molecules of $H_2O$ in water:—*water I*, tridymite-ice-like, rather rare, present to a certain degree at low temperatures below 4°C: *waterII*, quartz-like, predominating at ordinary temperatures: *water III*, close packed, ideal liquid, ammonia-like, predominating at high temperatures for some distance below the critical point at 374°C. These forms pass continuously into each other with change of temperature. Throughout, as G. W. Stewart has insisted, there is no question of a mixture of volumes with different structures; at all temperatures the liquid is homogeneous but the average mutual arrangements of the molecules resemble water I, II and III in more or less degree. The sequence of water I—II—III is one of increasing rotatory and translatory molecular movement and of the consequent diminution of the dipole forces of cohesion of the liquid and relative increase of the van der Waals component. It is a sequence of increasing fluidity but not one of increasing volume. The immediate effect of breaking down the relatively empty ice-like structure of water I is a decrease of volume to water II, followed by an increase of a more normal kind to water III, where the increase of the mean distance of the neighbouring molecules due to thermal agitation more than compensates for the geometrical contraction of the transition from the quartz-like to the close packed structures. The theory of polymorphic forms of water is familiar to chemists, particularly from the work of H. E. Armstrong. If the view put forward above is accepted it will be seen that these theories have a close relationship to the facts, but have been conceived too much in the manner of molecular chemistry. Trihydrol $(H_2O)_3$, dihydrol $(H_2O)_2$, and hydrol $(H_2O)$ have no direct structural analogy with water I, II, and III, but the latter explain, by means of the geometrical internal structure of the liquid, physical properties which the former attempted to explain in terms of hypothetical molecules.

**§4. Effects of high pressures**

These considerations may be supported by an examination of the behaviour of water under pressure. The equilibrium diagram of water, has been given by Bridgman.[9] At different pressures four kinds of ice, I, III, V, and VI are found in equilibrium with water. Their relative volumes (normal cold water 1.000) and that of the water in equilibrium with them, are shown in Table I. Ices III, V, and VI are all denser than water, showing that the latter has not a close packed structure.

In considering these equivalent volumes the effect of the compressibility of the water molecules themselves has to be taken into account. A rough way of doing this is provided by assuming that the volume change of any one ice at different pressures inside its range of stability is due to the compression of the atoms themselves (this is only strictly true for crystal structures without variable parameters). We thus interpret the volume ratio of any one ice over its extreme pressure range in Table I as the volume ratio of the water molecules over the same pressure range. In this way it is possible to determine what part of the actual loss of volume of water at high pressures is due to the compression of the molecules, (column 6, relative volume of water molecule), and what part to the crushing of the organized structure of the liquid, (column 7, geometrical equivalent volume of water). It will be seen that at the highest pressures, 10,000 atmospheres, this geometrical crushing amounts to 11 percent, though the volume is still 44 percent from that of the close packed structure of water molecules of radius 1.4A. The geometrical compression factor is far greater for ices III, V and VI than for water. The full meaning of this would only appear if the crystal structures of these forms could be determined by x-rays. The isomorphism between tridymite and ice I suggests forcibly that of the structures of ices

[9] Bridgman, Proc. Nat. Acad. Sci. **47**, 441 (1912).

TABLE I. *Equivalent volumes of water and various types of ice (Bridgman).*

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| Pressure atmospheres | Ice form | Ice volume (observed) | Equivalent water volume (observed) | Geometrical equivalent volume of ice | Relative volume of water molecule | Geometrical equivalent volume of water |
| 1 | I | 1.0900 | 1.0000 | 1.090 | 1.000 | 1.000 |
| 2000 | I | 1.0571 | 0.9253 | | 0.970 | 0.955 |
| 2000 | III | 0.8774 | | 0.905 | | |
| 3500 | III | 0.8636 | 0.8815 | | 0.956 | 0.922 |
| 3500 | V | 0.8085 | | 0.847 | | |
| 6000 | V | 0.7929 | 0.8472 | | 0.937 | 0.904 |
| 6000 | VI | 0.7636 | | 0.816 | | |
| 10000 | VI | 0.7385 | 0.8055 | | 0.906 | 0.890 |
| | | | | Observed vol. corrected for size of water molecule Col. 3/Col. 6 | From the change in volume of the preceding ice | Col. 4/Col. 6 |

III, V and VI, at least one must be that of quartz. However, this may be, the considerable diminutions of volume, 5 percent, 9 percent, and 11 percent on passing from water to ices III, V and VI respectively confirms the x-ray evidence that the structure of water is far from being a close packed one.

## §5. Evidence from Raman spectra

The nature of this difference is further brought out by studying the interaction with water of the longer electromagnetic waves. The Raman spectrum of water has been much studied. It consists of three bands at $\Delta\nu = 3216$, 3435 and 3582; these plainly correspond to the fundamental frequency $\nu = 3700$ of the $H_2O$ molecule found from the infrared absorption of water vapour. The water bands differ from those of other liquids by being so broad as to overlap almost completely. This indicates the effect of local dipoles in disturbing the term levels and itself is evidence for internal structure of a different kind from that of normal liquids. The lines corresponding to the water bands are shown in the Raman spectrum of ice at $\Delta\nu = 3193$, 3391 and 3549. This shows that to a first approximation the effect of neighbouring molecules on any molecule is the same in both phases, and that probably the structure of water is, like that of ice, a 4-coordinated tetrahedral one. That this coordination is not exact and tends to break down at higher temperatures is shown by the relative intensities of the lines. In ice the 3200 line is the predominant one, in cold water that at 3400 and in hot the 3600 line. The weakening of the 3200 line in the Raman spectrum is therefore a parallel indication with that of the 2.2A maximum in the x-ray diffraction, and marks the beginning of the transition to the close packed structure. It is tempting to identify the 3200, 3400, 3600 bands as corresponding respectively to the previously defined water structures I, II and III, but such a correspondence cannot be maintained until the nature of the transitions corresponding to these bands has been worked out.

There is also a shift towards the higher frequencies indicating weakening of the mutual polarization forces of the molecules in water relative to ice.

## §6a. The structure of ice

Before discussing the dielectric constants of water and ice it is necessary to examine closely the structure of ice. In the normal ice structure the positions of the H nuclei and consequently the orientations of the molecules are fixed. This follows from the x-ray determination of the

positions of the O atoms combined with the knowledge of the molecular structure derived from band spectra. Every molecule is surrounded by four others in a tetrahedron and this arrangement will have least energy if the H nuclei, which subtend an angle of about 109° at the centre of the molecule,* lie opposite two of the neighbours, while one of the H-nuclei of each of the remaining neighbours lies opposite a negative corner of the original molecule. (See Fig. 4.) Such an arrangement has, of course, no trigonal symmetry and is impossible at first sight to fit with the x-ray structure of ice.[3] But in the derivation of the latter, only the effects of the O atoms can be taken into account and so no structure leaving the positions of these unchanged can be rejected on x-ray grounds. The simplest of physically possible structures is shown in Fig. 6. It requires a cell three times as large as that proposed by Barnes, but is still of trigonal symmetry. It belongs, however, to a polar class, whereas Barnes' structure belongs to the holohedral class. The crystallographic evidence is conflicting, but the careful work of Adams[10] suggests that the polar class is the correct one, though often masked by twinning on the basal plane. The attempt by Dr. W. A. Wooster to prove the polar character of ice from its pyro-electricity by Martin's method[11] gave, however, negative results; this may have been due to twinning.

It is of course possible to construct regular ice structures without polar properties. For geometrical reasons, however, this implies a very large cell and extreme complexity: the simplest of these with the symmetry $C_3^2-C3$, still geometrically but not physically polar, contains 96 molecules in the unit cell. The formation of such a complex arrangement under ordinary circumstances is most improbable. The structure of Fig. 6 is the simplest *regular* structure for ice. Therefore it is quite conceivable and even likely that at temperatures just below the melting point the molecular arrangement is still partially or even largely irregular, though preserving at every point tetrahedral coordination and balanced dipoles. In that case ice would be crystalline only in the position of its molecules but glass-like in their orientation. Such a hypothesis may be still necessary to explain the dielectric constant and the absence of pyro-electricity.

### §6b. A theoretical discussion of the dielectric constants of water and ice

One of the most characteristic properties of water is its high dielectric constant, 88 at 0°C for frequencies up to $10^8$ cycles/sec. The dielectric constant of ice is sometimes thought of as being low. The difference between them is, however, largely a matter of the frequencies at which the dielectric constant is measured. The frequency variation of the dielectric constant for water and ice at different temperatures is shown in Fig. 7.

The nature of the dielectric constant as a function of frequency is much the same at all temperatures and apparently both for water and ice; the only important change is in the frequency scale for the different curves. For sufficiently low frequencies the dielectric constant of even quite cold ice can reach large values, possibly even values larger than the ordinary values for water. For sufficiently high frequencies the dielectric constant of water falls below its constant low-frequency value, but only at higher frequencies for higher temperatures. The value of the low frequency dielectric constant falls for water with rising temperature and probably for ice with falling temperature. The greatest values are reached for cold water (or perhaps warm ice). The most modern values are shown in Fig. 7a and some old low temperature values.

The dielectric properties of water and ice have been carefully analysed by Debye.[12] He uses a model consisting of spherical dipole carriers for the $H_2O$ molecules, free to rotate under the combined influence of the effective electrical field acting on them and the inner viscosity of the water or ice. This viscosity must be interpreted for the ice in a generalised sense. He shows that the form of the curves as functions

* The angle 103–106 given above on p. 517 refers to the angle between the H and O nuclei. Here the centre of the molecule is not its centre of mass near the O nucleus but its electronic centre, which is shifted toward the pair of H nuclei, see below p. 529.

[10] Adams, Proc. Roy. Soc. **A128**, 588 (1930).

[11] Martin, Mineral. Mag. **21**, 519 (1931).

[12] Debye, *Polare Molekeln*, Chapter V, (1929).

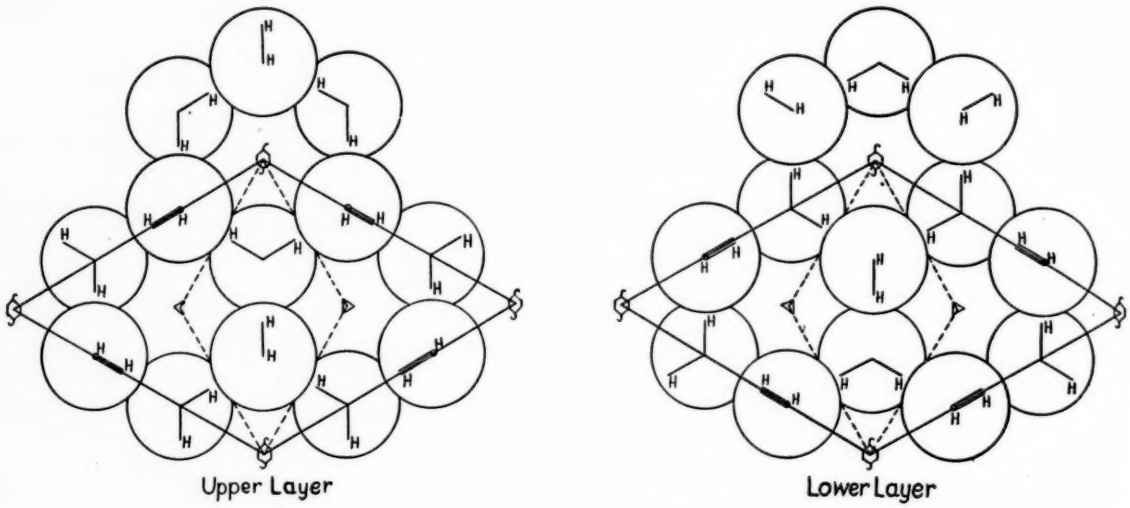
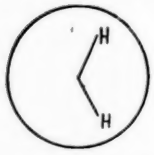



FIG. 6. Ice structure viewed along hexagonal axis.

Explanation: The structure* is shown in two layers; —— marks the edges of the true cell, $a=7.81$A; - - - - - marks the edges of Barnes' cell, $a=4.51$A.



Indicates in upper layer molecules, $(5/8)c=4.61$A above base of cell;
Indicates in lower layer molecules $-(1/8)c=-0.92$A above base of cell;
The two H lie above the O, and the OH directions are inclined at 10°16′ to the $c$ axis.

Indicates in upper layer molecules $(7/8)c=6.45$A above base of cell;
Indicates in lower layer molecules $(1/8)c=0.92$A above base of cell.
One H lies above O on the $c$ axis, the other below O at 70°16′ to the $c$ axis. In both cases the dipole axis points with its positive direction upwards, inclined at 54° to $c$ axis.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $6O_I$ at | $\frac{1}{3}$ | 0 | $\frac{1}{16}$ | $\frac{2}{3}$ | $\frac{2}{3}$ | $\frac{1}{16}$ | 0 | $\frac{1}{3}$ | $\frac{1}{16}$ |
| | $\frac{2}{3}$ | 0 | $\frac{9}{16}$ | $\frac{1}{3}$ | $\frac{1}{3}$ | $\frac{9}{16}$ | 0 | $\frac{2}{3}$ | $\frac{9}{16}$ |
| $6O_{II}$ at | $\frac{2}{3}$ | 0 | $\frac{15}{16}$ | $\frac{1}{3}$ | $\frac{1}{3}$ | $\frac{15}{16}$ | 0 | $\frac{2}{3}$ | $\frac{15}{16}$ |
| | $\frac{1}{3}$ | 0 | $\frac{7}{16}$ | $\frac{2}{3}$ | $\frac{2}{3}$ | $\frac{7}{16}$ | 0 | $\frac{1}{3}$ | $\frac{7}{16}$ |
| $6H_I$ at | $\frac{1}{3}$ | 0 | $\frac{1}{16}+3z$ | $\frac{2}{3}$ | $\frac{2}{3}$ | $\frac{1}{16}+3z$ | 0 | $\frac{1}{3}$ | $\frac{1}{16}+3z$ |
| | $\frac{2}{3}$ | 0 | $\frac{9}{16}+3z$ | $\frac{1}{3}$ | $\frac{1}{3}$ | $\frac{9}{16}+3z$ | 0 | $\frac{2}{3}$ | $\frac{9}{16}+3z$ |
| $6H_{I'}$ at | $\frac{1}{3}+y$ | 0 | $\frac{1}{16}-z$ | $\frac{2}{3}-y$ | $\frac{2}{3}-y$ | $\frac{1}{16}-z$ | 0 | $\frac{1}{3}+y$ | $\frac{1}{16}-z$ |
| | $\frac{2}{3}-y$ | 0 | $\frac{9}{16}-z$ | $\frac{1}{3}+y$ | $\frac{1}{3}+y$ | $\frac{9}{16}-z$ | 0 | $\frac{2}{3}-y$ | $\frac{1}{16}-z$ |
| $12H_{II}$ at | $\frac{2}{3}+y$ | $y$ | $\frac{15}{16}+z$ | $\frac{1}{3}$ | $\frac{1}{3}-y$ | $\frac{15}{16}+z$ | $y$ | $\frac{2}{3}+y$ | $\frac{15}{16}+z$ |
| | $\frac{2}{3}$ | $-y$ | $\frac{15}{16}+z$ | $\frac{1}{3}-y$ | $\frac{1}{3}$ | $\frac{15}{16}+z$ | $-y$ | $\frac{2}{3}$ | $\frac{15}{16}+z$ |
| | $\frac{1}{3}$ | $y$ | $\frac{7}{16}+z$ | $\frac{2}{3}$ | $\frac{2}{3}+y$ | $\frac{7}{16}+z$ | $y$ | $\frac{1}{3}$ | $\frac{7}{16}+z$ |
| | $\frac{1}{3}-y$ | $-y$ | $\frac{7}{16}+z$ | $\frac{2}{3}+y$ | $\frac{2}{3}$ | $\frac{7}{16}+z$ | $-y$ | $\frac{1}{3}-y$ | $\frac{7}{16}+z$ |

$y=0.105$ $z=0.037$

* The full description of the structure is as follows: hexagonal $a=7.82$, $c=7.36$, 12 molecules $H_2O$ per cell; space group $C_{6v}^3-C6mc$; atomic positions (somewhat idealised).

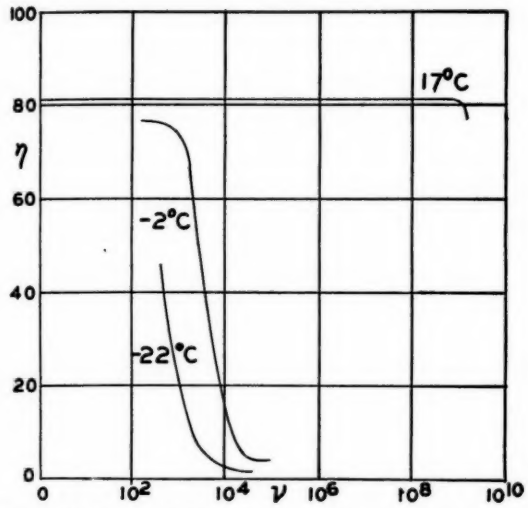



FIG. 7. Variation of the dielectric constant of water and ice with frequency (*International Critical Tables*).

of frequency are in surprisingly complete accord with this very crude theory. The inner viscosity, the relaxation time, and therefore the wave-length of the oscillations at which the great change of dielectric constant occurs, appear to increase discontinuously by a factor of $10^5$ on freezing, (this is perfectly natural), but otherwise the water-ice properties pass smoothly and continuously over into each other.

To this part of the discussion we cannot and need not attempt to add anything, but Debye does not analyse the absolute values of the low frequency dielectric constant as a function of

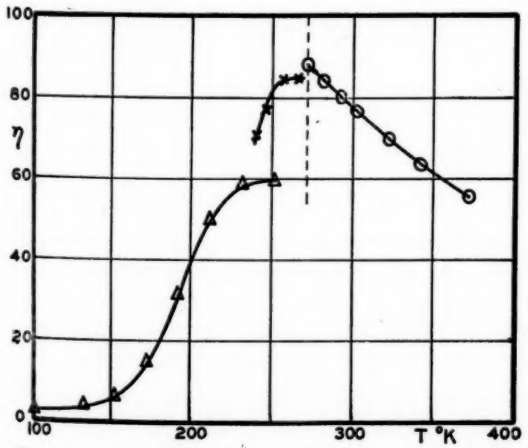



FIG. 7a. The dielectric constant of water and ice at low frequencies. Circle, Lattey, 1931; triangle, Fleming and Dewar, 1897; cross, Wintsch, 1932 (Helv. Phys. Acta V, 126 (1932)).

the temperature and we think that further insight can be obtained from such an analysis, by the same model.[13] It is essential to remember that this analysis uses Mosotti's hypothesis that the effective inner field strength at any point acting on one of our dipole carriers, is $E+(4/3)\pi P$, where $E$ is the electrical force (or intensity) and $P$ is the polarization of the medium. The applicability of Mosotti's hypothesis is open to question as is carefully pointed out by Debye. Its applicability is strictly only guaranteed by Lorentz'[14] lemma for completely random distributions of dipoles around any selected dipole or for distributions with cubic symmetry. These latter include distributions in which all the neighbours can be grouped into sets of four at the corners of regular tetrahedra whose centres lie at the selected molecule. For this model of rotating dipoles the Weiss-Langevin ferromagnetic theory applies in its simplest form so that—

$$P=N\mu L\left(\frac{\mu\{E+(4/3)\pi P\}}{kT}\right), \qquad (3)$$

where $N$ is the number of orientating dipoles, of moment $\mu$, per unit volume and $L(x)$ is Langevin's function,

$$L(x)=\coth x-1/x. \qquad (4)$$

From (3) and (4) it follows that for small fields

$$P\{1-4\pi N\mu^2/9kT\}=(N\mu^2/3kT)E,$$

or

$$P=[N\mu^2/3k(T-T_c)]E \quad (T_c=4\pi N\mu^2/9k). \qquad (5)$$

The dielectric constant $\eta$ is given by $\eta-1=4\pi P/E$, so that

$$\eta=1+4\pi N\mu^2/3k(T-T_c)=1+3T_c/(T-T_c). \qquad (6)$$

If all the water dipoles are freely orientable, then $N=6.06\times10^{23}/18$, $\mu=1.87\times10^{-18}$, $T_c=1200$. This is naturally impossible—it would correspond to a state of permanent polarization of ferromagnetic type. If we are to account for the observed values of $\eta(T)$ by an orientating dipole theory we must determine $T_c$ from (6) and the observed $\eta(T)$, and then $N$ from (5). We must, that is, use a variable number of effective freely rotating dipoles; this is *a priori* a perfectly acceptable conclusion. The actual

[13] See also Zwicky, Phys. Zeits. **27**, 271 (1926).

[14] Lorentz, *Theory of Electrons*, notes 54, 55.

effective numbers of freely rotating dipoles, expressed as a fraction of $N$, required to give the values of Fig. 7a are given in Table II. In these rough calculations the part of the dielectric constant to be referred to the orientations is taken as $\eta(T)-2$.

TABLE II. *Fraction f of orientable molecules required to account for* $\eta(T)$.

| *Water* | | *Ice* | |
|---|---|---|---|
| $T$°K | $f$ | $T$°K | $f$ |
| 273 | 0.220 | 270 | 0.216 |
| 293 | 0.235 | 250 | 0.200 |
| 325 | 0.26 | 225 | 0.178 |
| 350 | 0.28 | 200 | 0.154 |
| — | — | 175 | 0.118 |

These variations are in themselves entirely reasonable even if we can provide no special theory of them. They require us to assert that, from a 1/5 to a 1/4 of the water molecules or from a 1/10 to a 1/5 of the ice molecules must be regarded as free rotators in the sense of the theory. At the same time, the great bulk of the water or ice molecules must be definitely regarded as *not free to rotate*. This is in accord with the theory of water which we are developing here, but the proportion of *non-rotatable* molecules is perhaps rather far from unity, especially for crystalline ice. It is commonly held on the basis of a calculation by Debye[15] that so few ice molecules have to turn round in fields of any ordinary intensity (1 in 5,000,000 in a field strength of 1 volt/cm) that the ice lattice could not be upset. But this is not the same thing—what we have calculated is not how many turn but how many are really free to turn and perhaps this latter number is of more importance than Debye's number for the lattice stability.

We may summarize the discussion up to this point by admitting (1) that it is possible to accept a rotating dipole theory of the dielectric constant of water and ice without contradiction with the theory of the structure which we are discussing here, but (2) that there are inherent difficulties in a rotating dipole theory which requires us to accept it with caution if at all. These difficulties will become more prominent when we show below (p. 530) that the total energy of ice or water probably derives mainly from the interactions of dipoles not free to rotate (except for the irrelevant form of rotation about a dipole axis). But if the free dipole theory has to be abandoned or modified, it is probable that the dielectric constant can be derived from the re-orientation of blocks of polar crystal by the applied field. In water, the blocks would be very indefinite liquid crystals, very easily interconvertible; in ice the time of conversion would necessarily be longer and increase as the temperature falls. It is not yet necessary to attempt to construct such a theory in detail, but in some such way one might remove what seems to us to be the chief objection to the free dipole theory—namely that very small changes in $f$ correspond to enormous changes in dielectric constant, so that the factors determining $f$ ought somehow to be explicitly present in the theory.

[15] Debye, reference 12, p. 122.

## §7. A comparison of water with other liquids

The physical properties of water and ice seem all the more abnormal when compared with other compounds of similar electronic structure. The $H_2O$ molecule is of the neon type with ten electrons, as are also $CH_4$, $NH_3$ and HF. The significant properties of these substances are shown in Table III. For comparison the same properties are also shown for the hydrides of the second row elements $PH_3$, $SH_2$ and HCl, as well as for some hydrides of diatomic complexes such as CC, CN, CO, CF, NN, NO, OO. It can be seen at once that these substances fall into three classes. The majority are typically molecular with low critical and boiling points and short liquid ranges. Others like hyponitrous acid HNO, formaldehyde $H_2CO$ and acetylene HCCH, tend to polymerise. The remainder, $H_2O$, HF, $H_3COH$, $H_2NNH_2$, $H_2NOH$, $H_2O_2$ and HCN form the group of typical associated liquids with relatively high boiling and critical points and long liquid ranges. All these molecules except $H_2NNH_2$ possess single highly polar OH(FH, C−H) groups, and it is plainly the attraction between the positive end of these dipoles and the negatively charged remainder of the molecule that determines the extra cohesive forces in these cases. In HF the cohesion is better regarded as due not to dipoles but to "the H-

TABLE III. *Properties of simple molecular substances.*

| Substance | Crystal structure | Mol. vol. in liquid cuA | Melting point $T$°abs. | Boiling point $T$°abs. | Crit. temp. $T$°abs. | van der Waals constants $a$ | van der Waals constants $b$ | Latent heats kcal./g mol. Fusion | Latent heats kcal./g mol. Evap. | Viscosity at temp. $T$°C | Dielectric const. | Dipole moment |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | *CP* | 63 | 89 | 109 | 191 | 0.0036 | 0.00162 | 0.023 | | 0.0025, −34 | | 0 |
| $NH_3$ | *CP'* | 45 | 196 | 234 | 405 | .0080 | .00161 | 1.84 | 5.6 | 0.0179, 0 | 25.4 | 1.5 |
| $OH_2$ | *T* | 30 | 273 | 373 | 647 | .0118 | .00150 | 1.41 | 9.72 | Mobile | 80 | 1.87 |
| FH | *Pol* | 33 | 190 | 293 | | | | 1.09 | 6.02 | | 83.5 | |
| $PH_3$ | *CP'* | 76 | 140 | 188 | 327 | .0094 | .00233 | | | | | 0.55 |
| $SH_2$ | *CP'* | 63 | 187 | 211 | 373 | .0089 | .00193 | | 4.23 | 0.00435, −63 | 5.93 | 1.10 |
| ClH | *CP* | 65 | 160 | 190 | 325 | | | 0.050 | 3.54 | 0.00455, −45 | 8.85 | 1.03 |
| $H_3CCH_3$ | *HCP* | 110 | 102 | 184 | 305 | .0119 | .00312 | | | | | 0 |
| $H_3CNH_2$ | | 80 | | 267 | 430 | .0144 | .00272 | | | 0.00236, 0 | 10.5 | 1.31 |
| $H_3COH$ | | 65 | 175 | 338 | 513 | .0199 | .00318 | 0.052 | 11.0 | 0.0055, 25 | 34 | 1.73 |
| $H_3CF$ | | | | 195 | 316 | .0092 | .00235 | | | | | |
| $H_2NNH_2$ | | 52 | 274 | 386 | 653 | | | | | Viscous | | |
| $H_2NOH$ | | 44.5 | 306 | 340 † | | | | | | | | |
| HOOH | | 38.5 | 271 | 357 \|\| | | | | 0.25 | 12.3 | Viscous | 92.8 | |
| $H_2CCH_2$ | | 76 | 103 | 170 | 282 | .0089 | .00255 | | | | | 0 |
| $H_2CO$ | *Pol* | 61 | 181 | 252 | | | | | | | | |
| HNO | *Pol* | | Solid at 290 | Unstable | | | | | | | | |
| HCCH | *Pol* | 69 | | 191 | 308 | .0087 | .00239 | | | | | |
| HCN | | 64 | 259 | 300 | 457 | | | | 5.6 | 0.0026, −7 | | |

*CP* = cubic close packing.
*CP'* = polar modified cubic close packing.
*HCP* = hexagonal close packing.
*T* = tridymite structure.
*Pol* = Polymerises.
† At 60 mm Hg. Unstable at higher temperatures.
|| At 68 mm Hg. Unstable at higher temperatures.

bond." But even in this group water is unique. It has the highest van der Waals constant $a$ corresponding to the greatest intermolecular attraction, and the lowest $b$ corresponding to the smallest distance between molecular centres. This emphasises what we have tried to show above, that the peculiar cohesion of water is due not only to the presence of dipoles, but to the geometrical possibility of the fitting together of the molecules. It is only in water that the tetrahedral arrangement of molecules is possible. The presence of two and only two H atoms per molecule gives the possibility of attaching two molecules by this means, and two others by means of their own H atoms, thus mimicking the ionic structure of quartz with one H between every two oxygens instead of one oxygen between every two silicons (see Fig. 8).

Such a three dimensional self-perpetuating structure is impossible for ammonia with 3 H atoms and place for only one more, or for hydrofluoric acid with only one H atom. It is natural

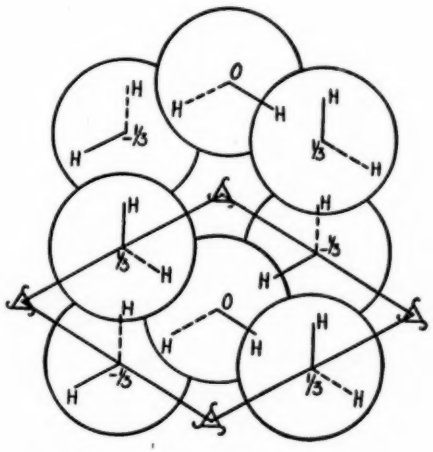
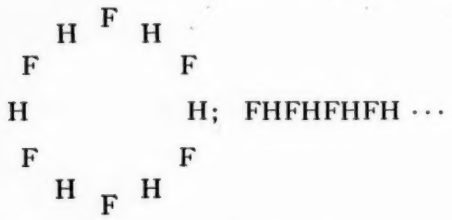


FIG. 8. "Quartz" water structure.

The molecules are in three layers, $-(1/3)c$, 0, $(1/3)c$ from the base of the cell. The OH directions pointing upwards are shown ——H. The OH directions pointing downward are shown - - - - H. The central atom shows the distorted tetrahedral coordination.

to suppose that in HF we have merely a linear dipole, that the tetrahedral skeleton is not developed and that the only point of attachment of another H is more or less opposite the first H. In that case we can only have a linear coordination and HF must form either rings or chains:—




In $NH_3$, or in HF if we should rather assume that the latent tetrahedron is still present, we can still only obtain single rings or chains. For example, in $NH_3$, we can have such a structure as in Fig. 9 in which the + signs denote H-nuclei and the O signs vacancies. If we wish to add

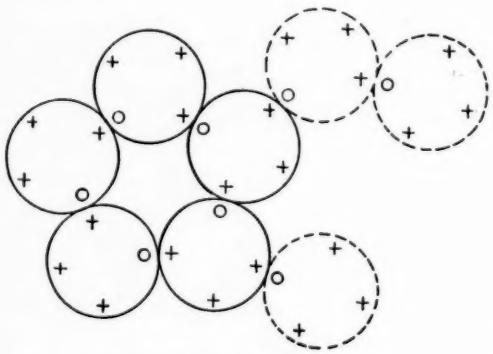


FIG. 9. Rings or chains in $NH_3$.

further molecules we can do so in the manner shown by the dotted circles, but these rays can never connect up again and must tend to loosen each other's attachments. The same diagram illustrates HF if + and O signs are interchanged. $H_2S$ with an internal structure similar to $H_2O$ has its H atoms too deeply buried to be effective as dipoles against the thermal rotation. Of all liquids, methyl alcohol most closely resembles water, but the apolar methyl group gives it a distinctly more molecular character. The coherent nature of liquid hydrazine ($H_2NNH_2$) cannot, however, be accounted for in any of the above ways. Its properties would repay more careful investigation. Two possibilities may be suggested: either H bonds can be formed between neighbouring molecules—though these have not so far been observed in N—H compounds, or the molecules in the liquid become zwitter ions $(H_3N)^+(NH)^-$ holding together by their electrostatic attraction.

We conclude, therefore, that the unique properties of water are due to a structure of the molecule which permits it to form in solid and liquid phases an extended electropolar complex characterised by tetrahedral (four) coordination.

## §8. The total internal energy of water

It is possible to give a rough quantitative check to this conception of the water structure. The total energy of water on this model is due mainly to the mutual potential between neighbouring molecules arising from their electropolar character. If the charge distribution in the $H_2O$ molecule were known, this could be calculated rigorously, but failing this, approximate values can be found by combining the information from spectra as to the mutual positions of the mass centres in the molecule, the value of the molecular dipole moment and the intermolecular distance calculated from the x-ray data.

If we take the spectroscopic model (Fig. 10) and place a charge $\epsilon$ at the $H$ positions and $-2\epsilon$ on the O nucleus we arrive at a molecule of dipole moment $5.6\times10^{-18}$ instead of the observed

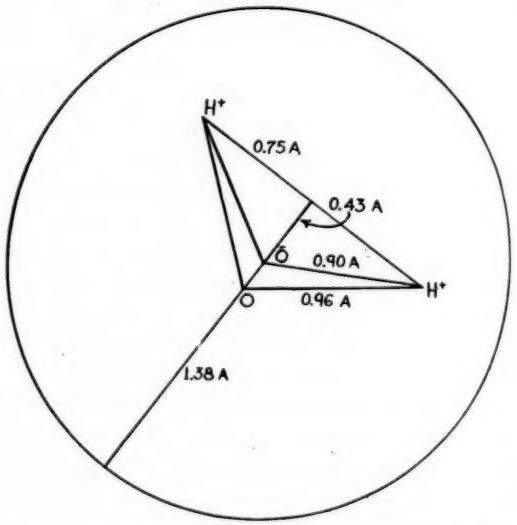



FIG. 10. The water molecule model. $H^+H^+$ are the hydrogen nuclei; O, the oxygen nucleus; $\bar{O}$ is the centre of negative charge and of the molecule.

$1.87\times10^{-18}$. It is clear that this discrepancy is due to having made no allowance for the effect of the two $H^+$ on the $O^{--}$ ion. This will be twofold. The centre of negative electronic charge will be moved from the O nucleus to some position intermediate between it and the H nuclei, and a certain concentration of negative charge will screen the H charges. The simplest assumption is to assume effective charges of $\epsilon'$ (less than $\epsilon$) at the H positions, and a charge $-2\epsilon'$ situated $x$A from the O nucleus on the bisector of the HÔH angle. With an electric moment of $2\times10^{-18}$ these are connected by the relation

$$(0.58-x)\epsilon'=0.21\epsilon.$$

This leaves only the choice of $x$ arbitrary between 0 and 0.37A. It is plainly nearer the former value because for six of the ten electrons of the system the negative centre must be very near the O nucleus. A value 0.15 for $x$, giving $\epsilon'=0.49\epsilon=2.33\times10^{-10}$ would not be unreasonable, and has the advantage for calculation of giving a tetrahedral arrangement of + and − charges.* Luckily we can find an entirely independent check on this value from the measurement of the dipole moment of hydroquinone. In this dihydroxy compound $HOC_6H_4OH$ the hydroxy groups rotate quite independently, and as they are symmetrically placed only the transverse electric moments $\mu_t$ are effective. (See Fig. 11.) By the theory of Fuchs[16] the observed moment $\mu$ represents the time average of the moments of end groups which neutralise each other in the trans and are additive in the cis position, and $\mu=2^{\frac{1}{2}}\mu_t$.

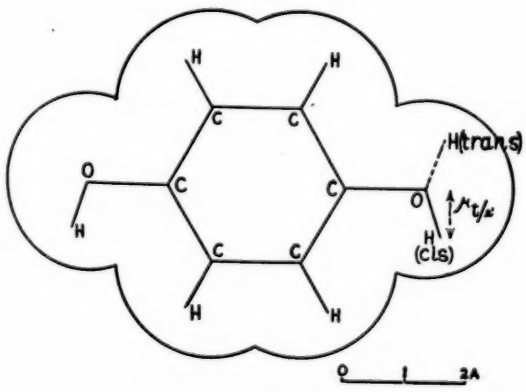



FIG. 11. Hydroquinone.

Now $\mu=2.34\times10^{-18}$ and therefore $\mu_t=1.66\times10^{-18}$. In our water model $\mu_t=0.75\epsilon'=1.75\times10^{-18}$. Thus the transverse moment derived from the model is 5 percent larger than that derived from the hydroquinone molecule. This difference of 5 percent is to be expected, as we have already assumed an increase of 5 percent, from 1.9 to $2.0\times10^{-18}$, in the direct moment, to allow for the effect of the polarising power of neighbouring water molecules.

We may therefore assume that the model of the water molecule is to a first approximation the correct one. It could be in fact derived purely from dipole moment measurements independently of spectroscopic data.

The mutual potential energy of two such molecules placed in such relations to each other as are found in ice (see Fig. 6) that is, with their centres $2.72\times10^{-8}$† apart and their effective OH directions making tetrahedral angles with each other, can be calculated by simple electrostatics. (In most cases these calculations were made graphically.) For the model chosen above this amounts to $0.533\times10^{-12}$ ergs in the mean. Actually there are three possible positions in ice satisfying these requirements: they may be called cis, trans, and skew arrangements, differing only in the azimuthal angular position of the two water tetrahedra in respect to the line joining them. The respective mutual potential energies can be found to be 0.504, 0.527, $0.551\times10^{-12}$ ergs per molecule pair. In any ice structure these types must occur in the ratio 1 : 1 : 2 and the mean weighted in this way is $0.533\times10^{-12}$ ergs per molecule pair. Every molecule has four neighbours, thus the potential energy per molecule is $1.066\times10^{-12}$ ergs, each molecule counting only once. This is equivalent to −15.3 kcal./g molecule.

In this calculation three factors have been omitted.

(1) *The mutual potential energy of molecules not in contact.* This is not very considerable. The mutual potential energy of two dipoles falls off as the cube of the distance, and owing to the

* In several of the subsequent calculations the value is taken as 0.5 for simplicity.

[16] Fuchs, Zeits. f. physik. Chemie **B14**, 339 (1931).

† The value of 2.76A at 0°C reduces by thermal contraction to 2.72A at 0°Abs.

mutual orientation contains approximately equal numbers of + and − terms. We need only consider next neighbours. A rough calculation gives for the potential energy due to the 13 next neighbours of an ice molecule $0.154\times10^{-12}$ ergs corresponding to +1.1 kcal./g.

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we can arrive at $B$ if $n$ is known from the equilibrium condition

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$F'(r)$ the electrostatic force between the molecules can be obtained graphically from the model. It is found to be $0.731\times10^{-4}$ dynes per molecule pair. $0.316\times10^{-4}$ dynes is the contribution of the van der Waals force, so that

$$\frac{n}{r_0}\frac{B}{r_0^n}=1.047\times10^{-4}\text{ dynes.}$$

Now $n$ cannot be very different from its value for the rare gases[19] $\approx12$ we have therefore

$$B/r_0^n=1.047\times2.72\times10^{-12}/12=0.238\times10^{-12}$$

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Introducing these corrections we have the *a priori* theoretical value for the energy of sublimation of ice at 0°K of $15.3-1.1+4.1-6.8=11.5$ kcal./g molecule. To compare with this we have the experimental value 10.70 kcal./g molecule for the heat of evaporation of water at 273°K. To this must be added (1) Latent heat of ice, 1.44 kcal./g mol. (2) $\int_0^{273}C_p(\text{ice})\,dT=1.28$ kcal./g mol. (3) $-\int_0^{273}C_v(\text{water vapour})\,dT=-1.61$ kcal./g mol. No account is taken of zero point energy or rotation in the solid. This gives an experimental value for the heat of sublimation of ice at 0°K of 11.81 compared with the theoretical 11.5 kcal./g mol. The closeness of the agreement is fortuitous as a change in the position of the effective molecular centre by as little as 0.05A would change the theoretical energy by 2.5 kcal./g mol.; a small change in the repulsive index* would produce an even greater effect. Nevertheless, the agreement is sufficiently real to show without doubt that by far the greater part of the cohesion of ice and also, therefore, of water at low temperatures is due to the electrostatic interaction of tripolar molecules in relatively fixed tetrahedral configuration.

This calculation is made for a regular structure without heat motion and therefore refers strictly only to ice at absolute zero. The energy of water is naturally greater, partly due to molecular movement, and partly to the breakdown of the regular four coordinated structure which proceeds more and more rapidly at higher temperatures until the critical point is approached

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### §9. Properties of ionic solutions: Density of solution and ionic hydration

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The simplest and possibly the most accurate method of estimating the real degree of hydration

TABLE IV. *Additional volume of uni-univalent salts in dilute aqueous solution, cuA per ion pair.*

| | $OH^-$ | Difference F−OH | $F^-$ | Difference Cl−F | $Cl^-$ | Difference Br−Cl | $Br^-$ | Difference I−Br | $I^-$ |
|---|---|---|---|---|---|---|---|---|---|
| $H^+$ | | | | | 29.3 | 9.5 | 38.8 | 20.3? | 59.1? |
| Difference Li−H | | | | | −0.8 | | −1.0 | | +2.7? |
| $Li^+$ | −8.3 | | | | 29.0 | 10.8 | 39.8 | 16.6 | 56.4 |
| Difference Na−Li | −0.9 | | | | −0.9 | | −0.4 | | +0.2 |
| $Na^+$ | −9.2 | +5.0 | −4.2 | 32.3 | 28.1 | 10.3 | 38.4 | 18.2 | 56.6 |
| Difference K−Na | +14.7 | | +17.6 | | +16.4 | | +17.1 | | +17.5 |
| $K^+$ | +5.5 | +7.9 | 13.4 | 31.1 | 44.5 | 11.0 | 55.5 | 18.6 | 74.1 |
| Difference Rb−K | | | +7.2 | | +8.0 | | +7.5 | | +7.7 |
| $Rb^+$ | | | 20.6 | 31.9 | 52.5 | 10.5 | 63.0 | 18.8 | 81.8 |
| Difference Cs−Rb | | | | | +11.9 | | +11.8 | | +11.2 |
| $Cs^+$ | | | | | 64.4 | 10.4 | 74.8 | 18.2 | 93.0 |
| $NH_4^+$ | | | 31.8 | 29.1 | 60.9 | 2.1 | 63 | 13.5 | 76.5 |

is the measurement of densities of ionic solutions. In sufficiently dilute solution the volume alteration per ion pair becomes constant. The value of this for certain salts is shown below (Table IV) calculated as additional volume in cubic A. It is at once apparent from the constancy of differences of rows and columns that the volume alteration is additive for ions. It is also apparent that the additional volume is roughly proportional to the ionic size. Assuming this and dividing the contribution of caesium chloride (for which the positive and negative ions have most nearly the same size) in proportion to their ionic volumes in the solid, we derive the apparent ionic volumes in water as shown in Table V. With the values of 27.4 for $Cs^+$ and 37 for $Cl^-$, the apparent ionic volume of other ions can be found. If the distribution of volume between $Cs^+$ and $Cl^-$ has been incorrect, all the volumes for positive ions will be too large and for negative too small, or *vice versa*, but relative values for either will be correct. The table shows a normal relation between volume in solution and in the solid only for $Rb^+$ and $Cs^+$ among positive ions and for all negative ions except $(OH)^-$ and $F^-$. All other cases show apparent volumes either

TABLE V. *Apparent ionic volumes in dilute aqueous solution.*

| Ion | Apparent vol. in solution obs.cuA per ion | Vol. in solution calculated from vol. in solid | Vol. of ion with $nH_2O$ observed vol. ($n$) | Vol. of ion with $nH_2O$ calculated from crystal data | Ion | Apparent vol. in solution | Ion | Apparent vol. in solution |
|---|---|---|---|---|---|---|---|---|
| $H^+$ | − 8 | 0.0 | + 51 (2) | + 39 | | | $(HS)^-$ | + 40 |
| $Li^+$ | − 8 | + 3 | +170 (6) | +150 | | | $(CN)^-$ | + 41 |
| $Na^+$ | − 8.5 | + 6 | +225 (8) | +180 | | | $(N_3)^-$ | + 52 |
| $K^+$ | + 8 | +15 | | | | | $(CNS)^-$ | + 72 |
| $Rb^+$ | +15.5 | +21 | | | | | $(NO_3)^-$ | + 38 |
| $Cs^+$ | +27 | +28 | | | | | $(CO_3)^{--}$ | + 7† |
| $NH_4^+$ | +12? | +18 | | | | | $(HCO_3)^-$ | + 45 |
| $Tl^+$ | | +21 | | | | | $(ClO_3)^-$ | + 61 |
| $Be^{++}$ | −42.4 | + 0.2 | + 77 (4) | + 74 | $Mn^{++}$ | −41 | $(BrO_3)^-$ | + 64 |
| $Mg^{++}$ | −48 | + 3 | +130 (6) | +150 | $Fe^{++}$ | −39 | $(IO_3)^-$ | + 42 |
| $Ca^{++}$ | −45 | + 7 | +133 (6) | +180 | $Co^{++}$ | −48 | $(SO_3)^{--}$ | + 28 |
| $Sr^{++}$ | −44? | +13 | +134 (6) | +230 | $Ni^{++}$ | −66 | $(SO_4)^{--}$ | + 39 |
| $Ba^{++}$ | −33 | +18 | +145 (6) | +270 | $Cu^{++}$ | −50 | $(SeO_4)^{--}$ | + 46 |
| $Al^{+++}$ | −87 | + 1.1 | + 91 (6) | +110 | $Zn^{++}$ | −56 | $(H_2PO_4)^-$ | + 55 |
| | | | | | $Fe^{+++}$ | −77 | $(MnO_4)^-$ | + 80 |
| $(OH)^-$ | − 2 | +15 | + 28 (1) | + 34 | $Cr^{+++}$ | −93 | $(CrO_4)^{--}$ | + 45 |
| $F^-$ | + 6 | +15 | + 36 (1) | + 34 | | | $(MoO_4)^{--}$ | + 59 |
| $Cl^-$ | +37 | +37 | | | | | $(WO_4)^{--}$ | + 54 |
| $Br^-$ | +47.5 | +47 | | | | | $(S_2O_3)^{--}$ | + 85 |
| $I^-$ | +66 | +66 | | | | | $(Cr_2O_7)^{--}$ | +139 |
| | | | | | | | $(SiO_3)^{--}$ | + 9† |
| | | | | | | | $(VO_3)^{--}$ | + 53 |

Data from Landolt-Bornstein referred to 20°, most values rough.
† Low values due to $(OH)^-$.

much smaller than in the solid or actually negative. The conclusion almost forces itself that in the first case the ions are not hydrated, and in the second they are to a greater or less degree. The open structure of water postulated above will obviously lead to a reduction in volume if it is disturbed by the permanent aggregation of several molecules around a single ion. If an ion is completely hydrated it will carry a number of water molecules around it, determined by Goldschmidt's coordination number. That is, the maximum hydration will be limited by the number of water molecules which can be packed in mutual contact around the ion. This depends only on the ionic radius. The theoretical coordination number of the different ions with water is shown in column 2 of the Table VI. This coordination number is, however, not only theoretical, but empirically observed as water of crystallisation in known crystal structures. These conclusions are reinforced by an examination of water of crystallisation. Water exists in crystals in three forms, (1) Structural water, water existing in holes, tubes or sheets in an otherwise rigid ionic structure, which can be driven off by heat without necessarily disrupting the structure, for example in the zeolites. (2) Ice, in polyhydrates such as $Na_2CO_3.10H_2O$ in which the ions are the dispersed phase. Such crystals are said to melt in their own water of crystallisation. (3) Coordinated water, in which the water molecules are grouped around particular ions. This is the only type that concerns us here. Taking only crystals of known structure into account we find the coordination numbers and only the coordination numbers shown in brackets in column 4, Table V. Assuming this coordination number we can calculate the apparent volume in solution occupied by the hydrated complex, by adding the values of column 1 to $n$ times 29.7, the volume occupied by each natural water molecule. This is shown in column 4. We can compare this with the volume of the coordination spheres of the same ions as they occur in crystals. This volume is shown in column 5. The agreement is fairly good except for the large divalent ions $Sr^{++}$, $Ba^{++}$, when the approximation of a coordination sphere is only an extremely rough one which overestimates the volume actually occupied. In general we may say that the examination of the specific gravity of solutions shows some ions to be completely hydrated and some unhydrated.

An attempt can be made to determine the degree of hydration theoretically starting from the model of water here developed. The hydration of an ion will occur when the potential energy of a water molecule forming part of the coordination shell round an ion is less than that of a molecule in free water. Now in free water, every molecule has four neighbours and a single molecule coordinated to an ion has three, the ion and two water molecules on the other side. This follows because the charge of the ion must be expected to attract the *two* H-nuclei or the *two* vacant places in the water molecule symmetrically and from the point of view of further coordination occupy them both. The condition for an ion having at least one coordinated water molecule is therefore that the potential energy for a water molecule due to the ion is less than that due to two other water molecules.*

The potential energy $P$ of a water molecule due to an ion depends only on the ionic radius and the charge. The values calculated for univalent ions are shown in Fig. 12. Taking 15 kcal./g ion as the electrostatic potential energy due to two water molecules, we can show that for univalent ions of radius greater than 1.6A no hydration is to be expected, while for all monatomic polyvalent ions, hydration will always occur. Where more than one water molecule is coordinated with an ion, a correction must be made for the mutual effect of these, which will always be in the direction of reducing the negative potential due to the ion and will be greater the larger the coordination number. The value of this correction can be calculated: it is given by $D_n[\mu^2/(r+r_w)^3]$ where $D_n$ is a purely geometrical factor depending only on $n$ the coordination number and tabulated below. $\mu$ is the dipole moment, $r$ and $r_w$ the radius of the ion and water molecule respectively.

* In the case of negative ions the considerations of §9a suggest that the coordinated water molecule may have three water neighbours; but for every negative ion except $F^-$ and $(OH)^-$ the potential energy of coordination is so small that there is no true hydration.

| $n$ | 2 | 3 | 4 | 6 | 8 | 12 |
|---|---|---|---|---|---|---|
| $D_n$ | 0.0625 | 0.334 | 0.573 | 1.188 | 1.99 | 3.89. |

This term is only significant for monovalent ions. Introducing it we can calculate the extra energy

$$n\{P-D_n\mu^2/(r+r_w)^3-15\}$$

due to coordinating an ion with 2, 3, 4, 6, ··· water molecules. It will be seen from Table VI that for $Na^+$, $K^+$, $F^-$ this is a maximum for $n=4$.* But 4 is the coordination number of water itself, therefore we may argue that the larger ions $Rb^+$, $Cs^+$, $Cl^-$, $Br^-$, $I^-$ with small or negative coordinating energy are in fact also 4-coordinated, to judge from their negligible volume alterations on solution. Hence *all monovalent ions are 4-coordinated in water solution*. Further evidence for this is given below.

TABLE VI. *Extra energy, kcal./ion, derived from coordination of water molecules on ions allowing for the effect of mutual interactions of water molecules. These figures do not represent experimental hydration energies.*

| Ion | $n=1$ | 2 | 3 | 4 | 6 |
|---|---|---|---|---|---|
| $Li^+$ | 15 | 28 | 39 | 46 | 49 |
| $Na^+$ | 11 | 21 | 29 | 33 | 28 |
| $K^+$ | 4.0 | 7.2 | 8.8 | 9.2 | 2.0 |
| $Rb^+$ | 2.6 | 4.6 | 5.6 | 4.9 | <0 |
| $F^-$ | 4.1 | 7.4 | 9.0 | 9.7 | 3.0 |
| $Cs^+Cl^-Br^-I^-$ | <0 | <0 | <0 | <0 | <0 |

The difference between the permanently hydrated $Li^+$, $Na^+$ ($K^+$, $F^-$) ions and the others is not geometrical but physical, the smaller ions carry with them through the water their permanently attached hydration shell; the larger ions on moving exchange water neighbours.

For divalent, and *a fortiori* for polyvalent, simple ions the coordination number is always the highest sterically possible, which is 6 for all rare gas and most 18-shell ions, except for $Sr^{++}$, $Ba^{++}$ which may be 8-coordinated. For these, however, owing to the greater effect of the water shell, there is very little gain of energy by changing from 6 to 8 coordination, and they seem generally to be found in the former state.

* $Li^+$ gives a maximum at $N=6$. But we have other reasons from crystallography and observed heats of solution to show that its coordination number is 4

### 9a. A calculation of the heat of hydration

When the potential energy of a molecule of water is lowered by being associated with an ion, this energy appears as an additional term in the heat of hydration of the ion.

If water were an ideal insulator of dielectric constant $\eta$ and an ion a conductor of radius $a$ and charge $z\epsilon$ the energy of hydration would be given by

$$\tfrac{1}{2}[(\eta-1)/\eta](z^2\epsilon^2/a).$$

As Debye[20] has pointed out, this will only hold if the field near the ion is less than the saturation field of the dielectric and therefore not for any monatomic ion in water. The critical radius $a$ inside which water no longer has true dielectric properties has been calculated by Debye to be 11A for monovalent, and 31, 57, and 88A for 2, 3, and 4 valent ions. The present theory of water suggests the definition of another critical radius $a'$ as the radius where the polarisation reaches the maximum value possible while retaining a tetrahedral structure, that is $4\pi n\mu/(3)^{\frac{1}{2}}$ or $136\times10^2$ volts per cm. Inside this sphere the water molecules are orientated no longer by their mutual dipole attractions, but by the ion. It may in fact be called the coordination sphere of the ion. We would therefore expect the heat of hydration of an ion to be due to four terms.

(1) The energy of the coordination sphere proportional to the number of water molecules coordinated, and to the mutual energy of ion and molecule, with certain corrections to be mentioned below.

(2) The energy of the intermediate sphere.

(3) The energy of the main body of water outside the Debye sphere.

(4) The mutual energy of water molecules reoriented in the neighbourhood of the ion must plainly be subtracted from the expression for the hydration energy.

For ions of known charge and radius the energy of the first and third of these terms could be calculated. To calculate the second involves a knowledge of the polarisation of water in fields approaching saturation, which is not known experimentally and is difficult to calculate on the present theory. We can get round the difficulty, however, by virtually abolishing the

[20] Debye, reference 12, Chapter 6.

intermediate sphere and assuming a sphere of radius $R_z$ of sharp discontinuity, inside which the energy is that of ionic coordination, while outside it is that of ordinary water. $R_z$ must naturally lie between $a$ and $a'$ *and be dependent only on the charge and not on the ionic size*, but its actual value can only be derived empirically. Making these assumptions we may therefore write for the energy of hydration $U_h$ of an ion the expression

$$U_h=\frac{\eta-1}{2\eta}\frac{z^2\epsilon^2}{R_z}+nP_{\text{eff}}(r)-u_w.$$

In this formula $R_z$ is the radius of the virtual saturation sphere depending only on $z$, $n$ the coordination number of the ion, $P_{\text{eff}}(r)$ the mutual potential energy of one ion and a water molecule in its sphere of hydration which depends on $r$ and $z$, and $u_w$, the electrostatic energy of the water molecules disoriented, a small term which may be taken as before as 31 kcal./g ion, the electrostatic energy of 1 water molecule in water (see p. 530). To a first approximation the $P_{\text{eff}}(r)$ is proportional to the potential energy $P$ of a water molecule due to a charge $z\epsilon$ at distance $r+r_w$ where $r$ and $r_w$ are the radii of the ion and water molecule respectively.

$P$ can be calculated from the molecular model of water. Its value in terms of $r$ is plotted in Fig. 12. The curves for + and − ions are prob-

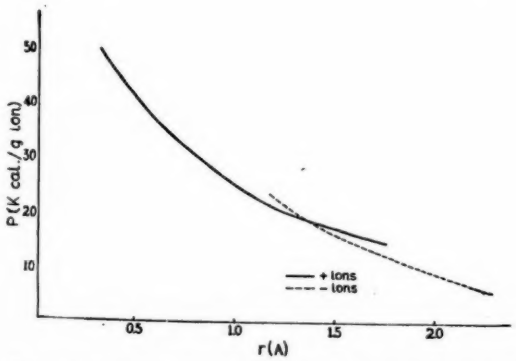


FIG. 12. Relation of ionic radius and mutual potential energy for water molecules and monovalent ions. For polyvalent ions, multiply $P$ by $z$.

ably not the same, as the water molecules arrange themselves in these two cases as shown in Fig. 13, a, b. The reason is that the $H^+$ in the water molecule is a definite centre of positive charges, while it is doubtful whether in the absence of another $H^+$, the molecule should be regarded as having two definite centres of negative charges rather than a general negative charge on the side remote from the $H^+$'s present. For most + ions the value of $P$ is sufficiently close to the simple dipole expression $\mu\epsilon z/(r+r_w)^2$.

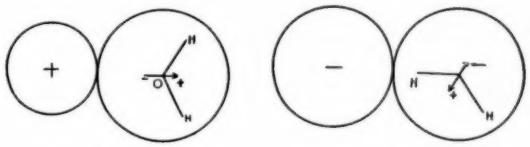


FIG. 13a, b. Orientation of water molecules with respect to positive and negative ions. $^-\!\!\longrightarrow\!\!^+$, Water molecule dipole.

The complete expression for $P_{\text{eff}}(r)$ on the present theory is

$$P_{\text{eff}}(r)=P\left\{1-F(r+r_w)+\frac{C}{(r+r_w)^4}+\frac{K\epsilon z}{(r+r_w)^2}-\frac{D_n\mu}{(r+r_w)\epsilon z}\right\}.$$

The correcting terms in the bracket are:

$F(r+r_w)$ to allow for the repulsion between ion and water molecule.

$C/(r+r_w)^4$ to allow for van der Waals attraction.

$K\epsilon z/(r+r_w)^2$ to allow for the change of dipole moment in the field round the ion ($K=d\mu/dE$).

$D_n\mu/(r+r_w)\epsilon z$ to allow for the mutual potential energy of the water molecules in the coordination sphere of the ion. $D_n$ is the geometrical factor tabulated on p. 533.

Of these terms $F(r+r_w)$ is difficult to estimate, and the value of $K$ is not known, so that no attempt will be made to calculate $P_{\text{eff}}(r)$ exactly.

However, a qualitative consideration of the terms in the bracket shows that they tend to compensate each other for different values of $r$. The ratio $P_{\text{eff}}(r)/P=p_z$ will not be very different from 1, and will be approximately constant for the same value of $z$, increasing with higher $z$ owing to the predominance of the polarisation term $K\epsilon z/(r+r_w)^2$. The actual value of the ratio can best be determined empirically. For this we use

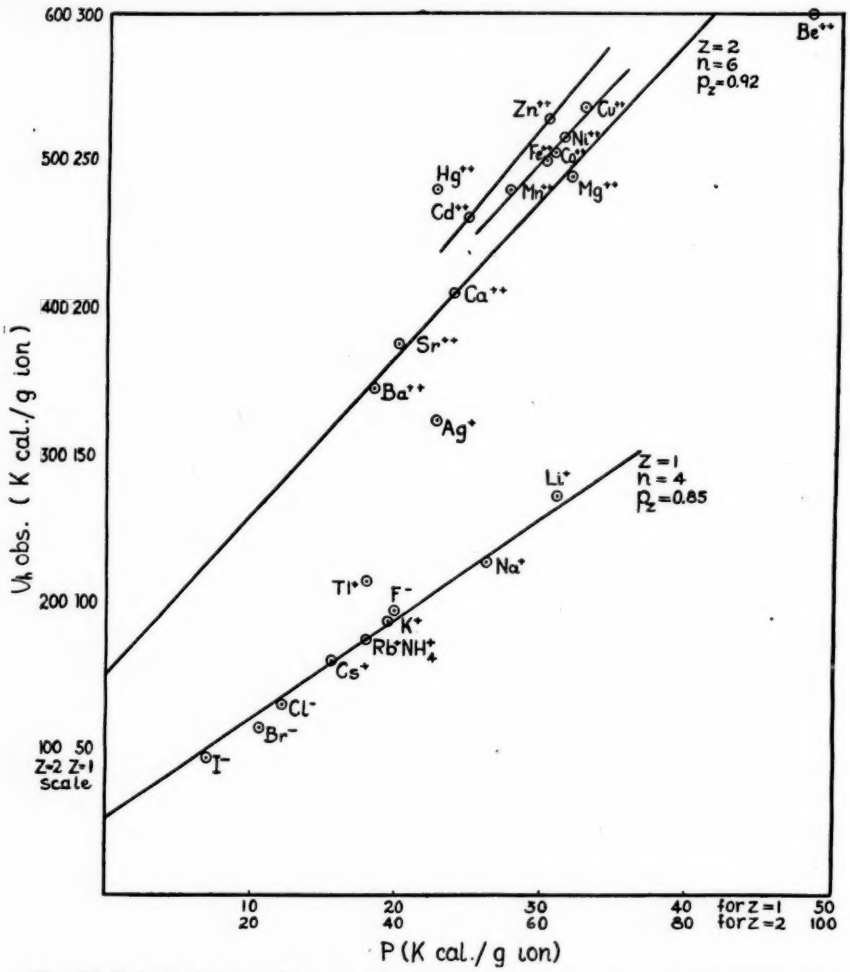


FIG. 14. Relation between heat of solution of ion $U_h$ and mutual potential energy with water molecule $P$. Details for ions of charge 1 and 2. (Values for the latter are plotted $\frac{1}{2}$ scale.)

the simplified expression

$$U_h=\frac{\eta-1}{2\eta}\frac{z^2\epsilon^2}{R_z}+np_zP(r)-u_w.$$

This on expressing $V_h$ as a function of $P(r)$ is of the simple form

$$U_h=a+bP(r)$$

where $a$ and $b$ are functions of $z$ only. If we attempt to check these theoretical considerations by comparison with experiment we are met at the outset by the difficulty that the absolute heats of the hydration of ions are not known, and cannot be directly measured. What can be observed is only the sum of heats of hydration of opposite signs, as when a salt is dissolved in water. For example for a metallic halide $M^+X^-$

$$U_h(M)+U_h(X)=U_{MX\ \text{cryst}}+U_S$$
$$=Q_{MX\text{aq}}+D_X+S_M-E_X+I_M,$$

where $V_{MX}$ is the lattice energy and $V_S$ the heat of solution of the salt; $Q_{MX\text{aq}}$ is the heat of formation of the aqueous salt at infinite dilution from $[M]$ cryst and $X_2$ gas; $S_M$ the heat of sublimation and $I_M$ the ionisation potential of the metal; $D_X$ the heat of dissociation and $E_X$ the electron affinity of the halogen. For monovalent salts the calculations of Meyer[21] and Sherman[22] have been extensively used. For others, calculations have been made from data in the Int. Crit. Tables. As in the problem of the

[21] Meyer and Helmholtz, Zeits. f. Physik **75**, 19 (1932).
[22] J. Sherman, Chem. Rev. **11**, 93 (1932).

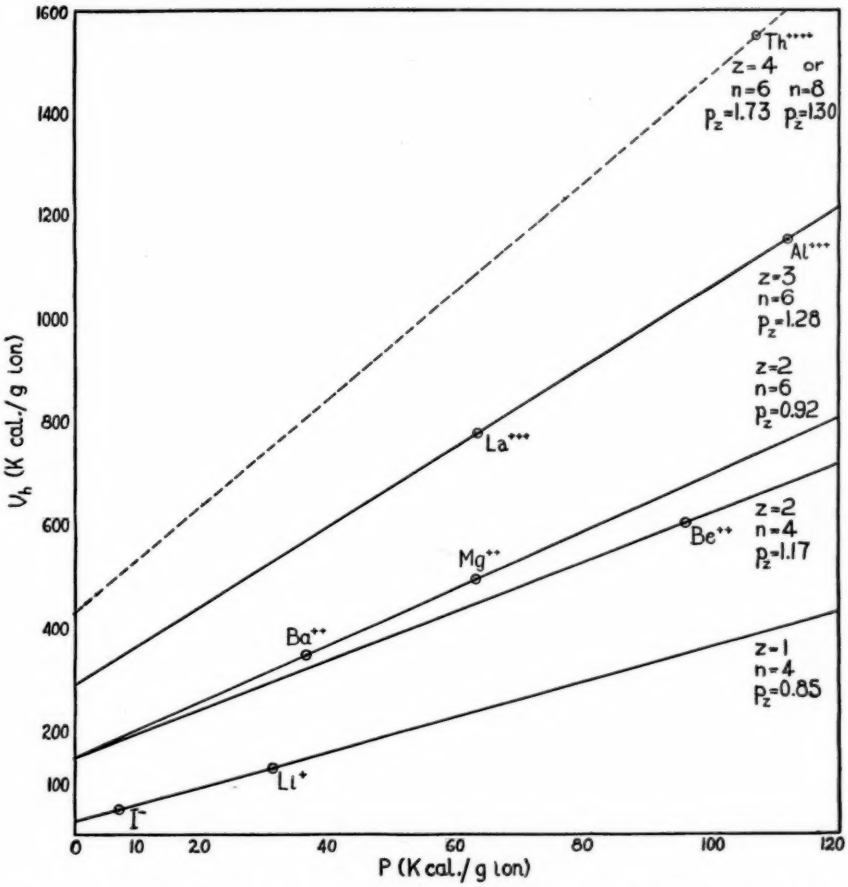


FIG. 14a. Relation between heat of solution of ion $U_h$ and mutual potential energy with water molecule $P$. General scheme.

determination of ionic radii the knowledge of one absolute ionic heat of one ion will give that of all the others. Attempts to assign such values have been made by Fajans[23] and Webb.[24]

Webb's treatment is much more thorough mathematically than that attempted here. However, being put forward before accurate values of atomic and molecular radii were known, it is essentially a theory treating water as a continuum of variable dielectric properties. It is interesting to note that by quite independent method he arrives at a value 82 for the heat of solution of $K^+$ instead of the 94 found here. If our arguments are granted this makes all his values for positive ions too low, and for negative ions too high.

Here we can proceed directly from our theory. For ions of opposite sign but the same valency $U_h$ can only depend on the radius $r$. Two ions of the same radius will have approximately the same heat of solution. Such a pair is furnished by $K^+$ and $F^-$ with empirical radii 1.33A for both. (Goldschmidt's empirical radii are used throughout as more directly applicable than those of Pauling or Zachariasen). The corresponding values of $P$ are 17.5 and 18.0 kcal./g ion. The value $U_h(K^+)+U_h(F^-)$ is 191 kcal./g ion pair. We may therefore take $U_h(K^+)$ as 94 and $U_h(F^-)$ as 97. With these values $U_h$ can be plotted against $P$. For any values of $U_h(K^+)$ or $U_h(F^-)$ the points for + and − ions lie on parallel straight lines. The above values were chosen to make all the points fall as near as possible to one line. Fig. 14. Any error must be small, and affect ions of the same charge by a constant term. The experimental results shown in Figs. 14 and 14a amply confirm the theory

[23] Fajans, Zeits. f. Elektrochemie **34**, 502 (1928). **34**, 546

[24] Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

sketched above. For all rare gas ions of the same charge, the points lie on one straight line whose slope gives $np_z$ and whose intersection with the axis of $U_h$ gives

$$\frac{\eta-1}{2\eta}\frac{\epsilon^2 z^2}{R_z}-u_w.$$

The values of $n$, $R_z$, and $p_z$ are given in Table VII, and using these values the observed and

TABLE VII. *Constants in equation for heats of solution of ions. $R_z$ and $a$ are given in Angstroms.*

| $z$ | 1 | 2 | | 3 | 4 | |
|---|---|---|---|---|---|---|
| $n$ | 4 | 4 | 6 | 6 | 6 | 8 |
| $p_z$ | 0.85 | 1.17 | 0.92 | 1.28 | (1.73) | (1.30) |
| $R_z$ | 2.9 | 3.6 | | 4.6 | (5.7) | |
| $a$ | 11 | 31 | | 57 | 88 | |

$u_w$=31 kcal./g ion.

calculated values for $U_h$ are given for all rare gas ions in Table VIII. The agreement is inside the experimental error in most cases. The greatest sources of error for the experimental values are in the heats of vaporisation of the metal, and in some cases in the ionisation potentials. For $Be^{2+}$, $La^{3+}$, $Th^{4+}$, the heat of vaporisation has been estimated from the melting point, while for $Fe^{3+}$ and $Th^{4+}$ the ionisation energy has been guessed at by analogy from similar atoms. No reliance must therefore be placed on the data for $3^+$ and $4^+$ ions which are only put in to show how they conform to the general scheme.

The only apparent exception to the linear law for ions of the same valency is for $Be^{++}$. This may be due to incorrect heat of vaporisation, but more probably to the fact that $Be^{++}$ is 4-coordinated and is the only representative of such a divalent ion.

As might be expected the 18 electron shell and the paramagnetic ions do not conform to the simple laws for rare gas ions, but have consistently higher heats of hydration. This is in perfect accordance with Goldschmid's views that such ions exert an extra polarising effect due to electronic interaction for which opportunity is provided by low lying excited states.

It is extremely interesting to note that, as far as can be seen, the points for $Mn^{++}$, $Fe^{++}$, $Co^{++}$, $Ni^{++}$, $Cu^{++}$ and $Zn^{++}$, $Cd^{++}$ (but not $Hg^{++}$ which is probably not fully ionised) lie on two lines nearly parallel to the rare gas ion line, and can be made to fit the general formula by the addition of a constant term to $P$ of $P_{mag}=4$ kcal./g ion for the first group and $P_{18}=8$ kcal./g ion for the second.

TABLE VIII. *Heats of solution of ions in kcal./g ion.*

| Ion | Ionisation energy ‖ | $U_h$ obs. | $U_h$ calculated |
|---|---|---|---|
| $H^+$ | 313 | 276 | |
| $Li^+$ | 124 | 136 | 131 |
| $Na^+$ | 118 | 114 | 116 |
| $K^+$ | 99.6 | 94 | 92 |
| $Rb^+$ | 95.9 | 87 | 87 |
| $Cs^+$ | 89.4 | 80 | 79 |
| $NH_4^+$ | | 87 | 87 |
| $OH_3^+$ | | | 130 |
| $OH^-$ | | | 105 |
| $F^-$ | 98.5† | 97 | 94 |
| $Cl^-$ | 92.5† | 65 | 67 |
| $Br^-$ | 87.1† | 57 | 63 |
| $I^-$ | 79.2† | 47 | 49 |
| $Be^{++}$ | 633 | 608 | ≈ 600 |
| $Mg^{++}$ | 521 | 490 | 495 |
| $Ca^{++}$ | 413 | 410 | 410 |
| $Sr^{++}$ | 384 | 376 | 370 |
| $Ba^{++}$ | 349 | 346 | 350 |
| $Al^{+++}$ | 1220 | 1149 | 1149* |
| $Sc^{+++}$ | 1020 | | 980 |
| $V^{+++}$ | 910 | | 830 |
| $La^{+++}$ | 833 | 768 | 768* |
| $Th^{++++}$ | ≈1600 | ≈1540 | 1540* |
| $Ag^+$ | 174 | 162 | |
| $Tl^+$ | 140 | 107 | |
| $Mn^{++}$ | 534 | 479 | |
| $Fe^{++}$ | 561 | 500 | |
| $Co^{++}$ | 580 | 504 | |
| $Ni^{++}$ | 594 | 516 | |
| $Cu^{++}$ | 645 | 536 | |
| $Zn^{++}$ | 626 | 528 | |
| $Cd^{++}$ | 596 | 462 | |
| $Hg^{++}$ | 672 | 480 | |
| $Fe^{+++}$ | ≈1346 | 1185 | |
| $In^{+++}$ | 1210 | 980 | |

* Used to determine $p_z$ and $R_z$.

† Electron affinity.

‖ Energy required to remove in succession the proper number of electrons.

If more data were available on heats of formation and solution, a number of further regularities might appear, particularly for the ions of the rare earths.

A more general and fairly obvious implication emerges from a consideration of the heats of hydration of ions. The heat of hydration is never much less than the ionisation potential of the ion. Physically this means that the function of the ionising medium is simply to return to the ion its missing electrons. This is primarily

effected by the coordination shell, which for all polyvalent ions contributes the greatest part of the energy of hydration. We now can see the reason for the persistence of liquids and solids of such ion hydrates as $Be(OH_2)_4^{++}$, $Al(OH_2)_6^{+++}$ which have as much right to be considered as complex ions as $PtCl_4^{--}$ or $Fe(CN)_6^{4-}$.

### §10. The effect of dissolved ions on the structure of water

The effect of the hydration of ions on the properties of the water in which they are dissolved is well shown by the work of Fajans' on the refractivity of ionic solutions. He finds that the effect on refractivity is an additive one for ions, but that while some ions give refractivities in solution similar to those expected for the free ion or in the solid crystal, others—precisely those which we have seen to be hydrated, such as $Li^+$, $Ca^{++}$, $Al^{+++}$—show negative values only explicable by the lowering of the refractive index of the solvent water by the coordination of water molecules round these ions.

The simplest way of considering the effect of ions on solvent water is in relation to the degree of disorder of the molecules. This is brought out by the observations of x-ray diffraction[5] and Raman spectra[25] of solutions. In both cases the addition of ions such as $Li^+$ or $H^+$ produces sharpening of lines and intensity shifts corresponding to more regular arrangement—i.e., one further back in the series:—Water I→II→III. The observations are not numerous or reliable enough for quantitative treatment, but the indications are overwhelming that small ions increase the regularity of the water arrangement.

This effect is shown in another way by the viscosity of ionic solutions. The viscosity of a solution is a complex effect but its nature is well brought out by the viscosity concentration curve of CsCl, Fig. 15. For dilute solutions at low temperatures there is first a decrease of viscosity with increasing concentration which afterwards changes to an increase. At higher temperatures no such decrease is observed and it is entirely lacking at all temperatures for salts of small ions such as LiCl or $CaCl_2$. Three factors may be thought of as contributing to the viscosity of ionic solution.

(a) The ions considered as independent massive particles carry momentum from one part of the liquid to another by their Brownian movement. This term will be proportional to the concentration, as the mean free path is independent of concentration, and probably to some small power of the temperature as in the case of gases.

(b) The ions, however, are not strictly independent and the lattice formed by them on the Debye-Hückel theory will present a certain resistance to shear which will appear as viscosity. This effect might be expected to increase with some high power of the concentration but to decrease exponentially with the temperature.

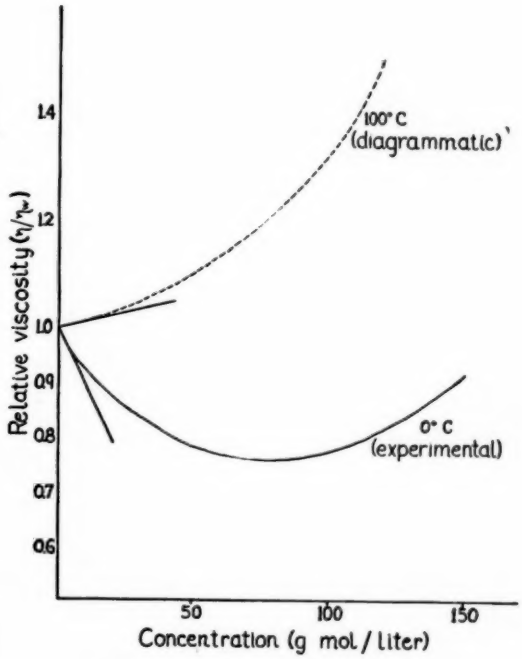


FIG. 15. Viscosity of CsCl solutions.

(c) The ions affect the water molecules in their neighbourhood, loosening or tightening the structure as already explained. A looser structure due to unhydrated ions will give rise to lower viscosity than pure water; a tighter structure, due to hydrated ions, a higher viscosity.

This term might be expected to depend linearly on the concentration, for low concentrations,

[25] Ganesan and Venkatewaran, Ind. J. Phys. **4**, 195 (1929).

and to be largely independent of the temperature.

The viscosity of an ionic solution of the salt $AX$ might therefore be written (this $\eta$ will not be confused with the former)

$$\eta(AX, C, T) = \eta(\text{aq}, T) - f_{(a)}(M_A, M_X)CT^{\frac{1}{2}} - f_{(b)}(C, z)e^{-\alpha/T} - f_{(c)}(r_A, r_X, z)C.$$

Here

$\eta(AX, C, T)$ is the viscosity of a solution of $AX$ of concentration $C$ and temperature $T$;

$\eta(\text{aq}, T)$ that of water at the same temperature;

$f_{(a)}(M_A, M_X)$ is the Brownian coefficient depending essentially on the masses of the ions and always positive;

$f_{(b)}(C, z)$ is the Debye-Hückel function depending on the charge of the ions and concentration, also always positive;

$f_{(c)}(r_A, r_X, z)$ is the "structural temperature" function depending on the ionic radii and the charge of the ions and able to have positive or negative values.

For low temperatures and low concentrations $f_{(c)}$ will be the principal term; for high concentrations, $f_{(b)}$; and for high temperatures, $f_{(a)}$. This qualitative hypothesis fully accounts for the shape of the CsCl curves. As far as $f_{(c)}$ is concerned the addition of a hydrated or non-hydrated ion is equivalent to that of a fall or rise of temperature. Following up this idea we arrive at the concept of the *structural temperature* of an ionic solution defined as that temperature at which pure water would have effectively the same inner structure, and therefore the same viscosity (x-ray diffraction, Raman spectrum, etc.). Naturally this can only apply to dilute solutions of strong electrolytes where the interaction of the ions and the momentum carried by their Brownian motion can be neglected. Both these factors tend to increase the viscosity at higher concentrations while the latter is the predominating effect at higher temperatures.

The change in the structural temperature of the solvent is seen most directly by the effects of ionic solutions on the temperature of the maximum density of water. The effect is always a lowering of the temperature of maximum density, that is, a raising of the structural temperature, but it is much smaller for the chlorides with small ions $H^+$, $Li^+$, $Mg^{++}$, than for those with large ions, and it is clear that here the increase is due to the $Cl^-$ ions, while the positive ions either do not contribute or actually lower the structural temperature. Of course the change in the temperature of maximum density cannot be quantitatively identified with the change in structural temperature, but it is satisfactory to observe that both vary in the same sense.

This conception of structural temperature may prove to be important in many physico-chemical fields, particularly where colloids are involved, as well as in many problems of bio-chemistry. It serves at once to show the reason for the antagonistic action of ions such as $Ca^{++}$ and $K^+$, the first lowering, the second raising the structural temperature. It is not, however, claimed to have a precise physical significance. It is only to a first rough approximation that the effect of adding an ion to a solution is that of a change in temperature. The real effect is not uniform, but gradually fades away at a distance from the ion, and it requires a much more rigourous theoretical treatment than that based on the crude model of the water molecule used above.

### §11. Introducing ionic mobilities again

The theory of ionic solution sketched above, though rendering many of our concepts more precise, does not add anything substantially new to the solution of the problem of ionic mobility. It must be possible, starting from a calculated hydration energy, or better still, from the observed heats of solution, to build up a hydrodynamical theory of the motion of an ion at infinite dilution. Such a theory would make precise the obvious qualitative relation between large hydration energy and small ionic mobility, but no attempt is made to derive it in this paper, for it would not help to solve our original problem.

What has emerged from the study of the molecular structure of water and ionic solution is that it offers no hope of a trivial explanation of the large mobilities of the $H^+$ and $(OH)^-$ ions. If we treat $H^+$ and $(OH)^-$ empirically as the other ions, the densities of their solutions indicate that they are hydrated (see Tables

IV and V). On the basis of this hydration low mobilities approximating to that of the $Li^+$ ion would be attributed to them. But other properties, particularly viscosities, show that $H^+$ and $(OH)^-$ do not behave normally. The effect of $H^+$ and $(OH)^-$ ions on the structural temperature is very large and negative. This shows that another mechanism than simple hydration must be involved, a mechanism that allows $H^+$ and $(OH)^-$ ions to move rapidly through the solution, and at the same time to impart to it a greater coherence. The second part of this paper is an attempt to describe such a mechanism, and so to explain the observed abnormal mobilities. We believe that the explanation presented is the only one possible, and further possible if, and only if the structure of water is substantially that described in Part I.

## Part II. A Quantum Mechanical Theory of the Extra Mobility of $H^+$ and $(OH)^-$ in Water

### §12. More exact statement of the problem

After the discussions of Part I it is impossible to accept the view that hydrogen positive ions are present in aqueous solution as naked protons. They must be firmly attached to at least one water molecule and the whole discussion may proceed on the assumption that the hydrogen positive ion is present in solution in the form $(OH_3)^+$, the oxonium ion, which like $(OH)^-$ and all other small ions will be more or less hydrated. The extra proton in $(OH_3)^+$ is no doubt accommodated at or near one of the two vacant tetrahedral positions among the electron orbits, the whole structure being very similar to the ammonia molecule $NH_3$.

Accepting this point of view which very simple considerations of energy are alone enough to demand, the exceptional mobility of this ion becomes all the more striking. If its mechanism of transport through the solution were the same as that of other ions, *which necessarily involve bodily transport of the identical ions to or towards the proper electrode*, it is impossible that its mobility should differ much from that of the ammonium ion $(NH_4)^+$ which it so closely resembles in electronic structure. But the observed mobility of $(OH_3)^+$ exceeds that of $(NH_4)^+$ by a factor of five. We conclude as above that a special mechanism must be acting both for $(OH_3)^+$ and $(OH)^-$, the ions of water in water, which is entirely distinct from bodily transport and this view which we shall develop leaves unaffected older views of the transport of any foreign ion through any solution. Whether an extra mobility is to be expected for the ions of any other solvent in that solvent is a matter for later examination. We shall see that special conditions must be satisfied, so that extra mobilities are likely to be uncommon, and in any case confined to ions in which the effective charge is derived from an extra or a missing proton.

An interesting confirmation of our view is provided by the mobility of $(OH_3)^+$ in hydrofluoric acid. Pure dry hydrofluoric acid does not conduct. Water present as an impurity acts as an electrolyte causing the formation of $(OH_3)^+$ and $F^-$ ions, more or less solvated of course. But $(OH_3)^+$ in liquid HF has a perfectly normal mobility.

We try here to describe the actual mechanism and its relation to the structure of water and think we have succeeded in a qualitative way. The fundamental idea which must be introduced is quantum mechanical. Having recognised the presence of $(OH_3)^+$ structures in the solution, quantum mechanics at once tells us that an $(OH_3)^+$ ion in sufficiently close contact with a water molecule $OH_2$ need not retain its extra proton but can transfer it to the other molecule. The proton jumps to and fro from one to the other when the configuration of the two molecules is favourable, and we show that this leads to a large extra drift down the field.

In formulating this problem we do not claim to have done more than restate ideas which must nowadays be commonplaces to every student of chemical physics. Similarly, in proposing our solution of the problem in its quantum mechanical dress we do not claim to have done more than attempt to render more precise ideas freely current in a vague form. Indeed, these ideas are of venerable antiquity for we really do little more than resuscitate in modern dress the idea of Grottius' chains. More recently Hückel[26] in work of which we were igno-

[26] Hückel, Zeits. f. Elektrochemie **34**, 546 (1928).

rant when we began this investigation has put forward the same idea of proton jumps. He has, however, not attempted to calculate the frequency of these jumps and has developed the discussion in such a way that it overlaps very slightly with ours. On the quantitative side one cannot claim to get very far—a quantitative explanation perhaps is hardly yet possible if any account is to be taken of the probable structure of water itself. But our discussion, equally with Hückel's, allows the conclusion that orders of magnitude are correct and that proton jumping is the essence of the extra mobility. Such other exceptional mobilities as are known appear to admit the same general explanation.

### §13. The mechanism of transport of $(OH_3)^+$ and $(OH)^-$

We have already stated that according to quantum mechanics an $(OH_3)^+$ ion in sufficiently close contact with a water molecule suitably orientated need not retain its extra proton. The reason is of course that there is another possible configuration of equal energy in which the extra proton has changed molecules. Further we may suppose that the three protons in $(OH_3)^+$ are in equivalent states, or if not, that there is an exchange degeneracy between them so that any one of the three is capable, at least in turn, of functioning as the detachable proton. If the two systems are at all far apart, or in an unsuitable relative orientation, there will be a considerable hill for the proton to jump through by the tunnel effect, and such transitions will be very rare. The great mass of the proton makes it entirely unable to penetrate barriers freely penetrable by electrons. But when the two systems are in close contact as neighbours in the water, and if they are so orientated that one of the protons (or the detachable proton) of $(OH_3)^+$ is nearly opposite some position in $OH_2$ into which it must move when it changes partners, the distortion of the electron orbits may well be such that only a small barrier hill survives, or the barrier may have almost totally disappeared, so that in either case the proton moves fairly freely from one system to the other during the period of this intimate contact.

In the absence of any external field we may conclude from the symmetry that, when the favourable conjunction is broken, the extra proton will be equally likely to be found on either of the original systems. Such exchange will lead to random migrations of the free protons and therefore of the apparent $(OH_3)^+$ systems through the solution, giving no net transport. On this view it is of course not the same proton, still less the same $(OH_3)^+$ system, that wanders about. But if there is an applied external field F, then the probability of the proton being found on separation attached to one or other of the two $OH_2$ systems will be slightly altered by an amount proportional to F (since the effect is a small one), that $OH_2$ system which lies in the region of lower potential energy for the proton being preferred. We will prove this rigorously for a simple model in §14. There will then be a steady drift of the apparent $(OH_3)^+$ ions down the potential gradient at a rate proportional to F, which exactly constitutes their observed extra mobility.

A very similar mechanism must hold for $(OH)^-$. In a favourable conjunction of $(OH)^-$ and another $OH_2$, a proton can pass from $OH_2$ to the $(OH)^-$ and the systems can separate again with the ion and neutral system interchanged. But it is clear that the two H's in $OH_2$ will lie slightly deeper in the electronic system than the three H's in $(OH_3)^+$ and have therefore somewhat less chance of making the exchange. Hence the smaller mobility.

It does not seem possible to prove *a priori* that these proton transitions *must* occur with the great rapidity demanded by the theory when the favourable configurations present themselves, but only that conditions may be such that they *can*. But we believe that we can argue backwards and assert first of all that the proposed mechanism of transfers certainly is *operative*—secondly that there is no other mechanism except bodily transport of the $(OH_3)^+$ complex through the medium which can convey appreciable mobility on the apparent oxonium ions and such bodily transport is known to be too slow. We may conclude therefore that the observed mobilities establish the sufficient rapidity of the transfers.

### §14. Approximate calculations

The form of the necessary approximate calculations for proton transitions from an $(OH_3)^+$

to an $OH_2$ neighbour was given some years ago by McCrea[27] in a tentative theory of electronic conduction. His work can be taken over with very slight changes, and represents physically just the right type of calculation for the process under discussion.

Two water molecules in a suitable configuration present two possible adjacent homes for the proton. Let the wave equation for the proton in one of these locations when isolated be

$$\nabla^2\chi+\kappa^2\{E-U(r_1)\}\chi=0 \qquad (\kappa^2=8\pi^2m_H/h^2) \quad (7)$$

with the normalized solution $\chi=f(r_1)=\psi$, $E=E_0$ for the state of lowest energy. We shall ignore the effect of excited states, a neglect which can be justified *a posteriori*. When two locations are available on neighbouring molecules we shall take the wave equation to be given to a sufficient approximation by

$$\nabla^2\chi+\kappa^2\{E-U(r_1)-U(r_2)\}\chi=0. \qquad (8)$$

with two solutions (to a zero order approximation)

$$\chi=f(r_1)=\psi; \quad \chi=f(r_2)=\varphi, \quad (E=E_0).$$

Solution $\psi$ means that the proton is on molecule 1, solution $\varphi$ on molecule 2. By familiar arguments the two lowest stationary states of this system are specified approximately by the wave functions

$$\chi_\pm=(\psi\pm\varphi)/q_\pm, \quad E=E_0+\epsilon_\pm \qquad (9)$$

where

$$q_\pm=\int\{2(1\pm(\varphi\psi))\}^{\frac{1}{2}}, \qquad (10)$$

$$\epsilon_\pm=(\bar{U}\pm U\dagger)/(1\pm(\varphi\psi)),$$

$$(\varphi\psi)=\int\varphi\psi d\tau, \quad \bar{U}=\int U(r_2)\psi^2d\tau, \qquad (11)$$

$$U\dagger=\int U(r_2)\varphi\psi d\tau.$$

$\int\cdots d\tau$ denotes integration over the whole configuration space of the proton. From the symmetry of these functions the proton in either stationary state is equally likely to be in either location.

[27] McCrea, Proc. Camb. Phil. Soc. **24**, 438 (1928).

Now let an electromotive force $F$ act on the proton in the direction of $x$ increasing, a direction which we shall for the present identify with the direction from the $\psi$-location to the $\varphi$-location. We take the origin of $x$ midway between the two locations and can then represent the perturbing potential energy for the proton by $-\epsilon Fx$. This perturbation may be assumed to be small compared with the perturbation due to the interaction of the two locations, and so may be applied as a new perturbation to the two states detailed in (9)–(11); but the interaction perturbation is itself so small that in calculating the new perturbation only these two close states need be taken into consideration. The perturbed wave equation is then

$$\nabla^2\chi+\kappa^2\{E-U(r_1)-U(r_2)+\epsilon Fx\}\chi=0, \quad (12)$$

and the perturbed solutions

$$\left.\begin{aligned}\chi_+{}^*&=\chi_+-\zeta\chi_- \quad (E=E_0+\epsilon_+)\\ \chi_-{}^*&=\chi_-+\zeta\chi_+ \quad (E=E_0+\epsilon_-)\end{aligned}\right\}, \qquad (13)$$

where

$$\zeta=\epsilon F\int x\chi_+\chi_-d\tau/(\epsilon_--\epsilon_+). \qquad (14)$$

There is no first order change in the energies. We can go further in evaluating $\zeta$, because

$$\int x\chi_+\chi_-d\tau=\int x(\psi^2-\varphi^2)d\tau/q_+q_-.$$

From the assumed symmetry of the field $U(r)$ and therefore of the wave function $\psi$ (or $\varphi$) of the fundamental mode it follows that

$$\int x\psi^2d\tau=-\tfrac{1}{2}R, \quad \int x\varphi^2d\tau=\tfrac{1}{2}R,$$

if $R$ is the distance apart of the centres of the two locations. Thus

$$\zeta=\epsilon FR/q_+q_-(\epsilon_--\epsilon_+). \qquad (15)$$

The general wave function for the perturbed system with time factors is therefore

$$\chi=\alpha(\chi_+-\zeta\chi_-)e^{-2\pi i(E_0+\epsilon_+)t/h}$$
$$+\beta(\chi_-+\zeta\chi_+)e^{-2\pi i(E_0+\epsilon_-)t/h}, \quad (16)$$

where $\alpha$ and $\beta$ are constants. This represents the progress of the system in time. If we chose $\alpha$ and $\beta$ so that $\chi=\psi$ for $t=0$, representing the

proton initialiy in the $\psi$-location, then (16) shows how it leaks over into the $\varphi$-location, and how it is on the average distributed between the two. One can use either method. We shall calculate the average distribution starting with the proton on $\psi$ (or $\varphi$) and deduce from this the average probability of a transition from $\psi \rightarrow \varphi$ (or $\varphi \rightarrow \psi$) being found on separation, which will be sufficiently accurate provided the state may be assumed to last long enough—that is for a time comparable to a half oscillation of (16).

For this purpose we express (16) in terms of $\psi$ and $\varphi$ and calculate $\overline{|\chi|^2}$, the time average of $|\chi|^2$, which is given by

$$\overline{|\chi|^2} = \alpha^2\left\{\psi\left(\frac{1}{q_+}-\frac{\zeta}{q_-}\right)+\varphi\left(\frac{1}{q_+}+\frac{\zeta}{q_-}\right)\right\}^2 + \beta^2\left\{\psi\left(\frac{1}{q_-}+\frac{\zeta}{q_+}\right)+\varphi\left(\frac{1}{q_-}-\frac{\zeta}{q_+}\right)\right\}^2. \tag{17}$$

Only terms to the first order in $\zeta$ need be retained. In order that $\chi$ may reduce to $\psi$ at $t=0$ we must have

$$\alpha = \tfrac{1}{2}(q_+ - \zeta q_-), \quad \beta = \tfrac{1}{2}(q_- + \zeta q_+).$$

With these values of $\alpha$ and $\beta$

$$\overline{|\chi|^2} = \tfrac{1}{2}\psi^2 + \tfrac{1}{2}\varphi^2(1+2\zeta(q_+^2-q_-^2)/q_+q_-) - \varphi\psi\zeta(q_+^2+q_-^2)/q_+q_-. \tag{18}$$

The $\varphi\psi$ term is symmetrical and represents an equal probability $\vartheta$ for the proton being in either location. Thus there is a probability $\frac{1}{2}-\vartheta$ that it will be found on $\psi$ and $\frac{1}{2}-\vartheta+\zeta(q_+^2-q_-^2)/q_+q_-$ that it will be found on $\varphi$. These probabilities add up to 1 so that

$$\vartheta = \tfrac{1}{2}\zeta(q_+^2-q_-^2)/q_+q_-,$$

which can be checked by direct calculation. Thus there are probabilities for the proton being left behind of

$$\tfrac{1}{2}(1-\zeta(q_+^2-q_-^2)/q_+q_-) \quad \text{on } \psi,$$

$$\tfrac{1}{2}(1+\zeta(q_+^2-q_-^2)/q_+q_-) \quad \text{on } \varphi.$$

There is therefore a probability

$$\tfrac{1}{2}(1+\zeta(q_+^2-q_-^2)/q_+q_-) \tag{19}$$

that the proton will be found, when the configuration is broken up, to have made a jump down the applied field when it starts on the up field molecule. Similarly when it starts on the down field molecule there is a probability

$$\tfrac{1}{2}(1-\zeta(q_+^2-q_-^2)/q_+q_-) \tag{20}$$

that it will be found to have jumped up field.

Any such jump effectively moves the oxonium ion through a distance $\Delta$, where $\Delta$ is the average distance apart of the $H_2O$ neighbouring molecules in water.* In a large number $N$ of such events, half will start with the proton up field and half with it down field. The oxonium ion will have effectively moved *down field* through the water after these $N$ events a distance $D$ given by

$$D = \tfrac{1}{2}N\tfrac{1}{2}(1+\zeta(q_+^2-q_-^2)/q_+q_-)\Delta - \tfrac{1}{2}N\tfrac{1}{2}(1-\zeta(q_+^2-q_-^2)/q_+q_-)\Delta,$$

$$= \tfrac{1}{2}N\Delta\zeta(q_+^2-q_-^2)/q_+q_-. \tag{21}$$

Written out in full, neglecting $(\varphi\psi)^2$ compared with 1, this becomes

$$D = \frac{N\Delta}{4}\,\frac{\epsilon FR\int\varphi\psi d\tau}{-\int\varphi\psi U d\tau+(\int\varphi\psi d\tau)\int U(r_2)\psi^2 d\tau}. \tag{22}$$

This formula can be used to give us the rate of movement of the effective hydrogen ion through the water in cm/sec. under unit potential gradient, which is equivalent to its mobility.

## §15. Numerical values

The value of the velocity of migration for the effective hydrogen ion under a potential gradient of F* volts/cm is given as $32.5\times10^{-4}$ F* cm/sec.[28] The value for the hydroxyl ion is $17.8\times10^{-4}$ F*. The value for the ammonium ion is the same as for the potassium ion, namely $6.7\times10^{-4}$ F*. Both the oxonium and hydroxyl ions must be expected to have an ordinary velocity of this order $6.7\times10^{-4}$ F* due to bodily transport through the fluid in the usual manner. They have

* It is necessary to recognize that by this simple jump the effective *charge* has not moved a distance $\Delta$ but of course only $R$; the movement $\Delta$ is as it were only consolidated if thermal agitation comes in and rearranges the dipole groupings sufficiently often. As has been pointed out to us by Frenkel in discussion, this thermal reorientation must be an integral part of the full description of the phenomenon which so far we have omitted for simplicity. We comment further on this aspect of a more exact theory at the end of §18.

[28] Lewis, *System of Physical Chemistry*, I, 212 (1918).

therefore an extra velocity due to the interaction mechanism of

$$(OH_3)^+;\ 25.8\times10^{-4}\ F^*\ \text{cm/sec.}$$

$$(OH\ )^-;\ 11.1\times10^{-4}\ F^*\ \text{cm/sec.}$$

The exact numerical values are not of importance. They refer to 291°K. It remains to be examined whether (22) can give comparable values when adjusted to correspond to the conditions in the solution.

(i) *Value of* $\Delta$. $\Delta$ represents the average distance apart of the $H_2O$ molecules in water when they are capable of interacting in this manner, one of them carrying the extra proton. For this distance we should probably take the average distance apart of the coordinated neighbours of Part I, $2.8\times10^{-8}$ cm.

(ii) *Value of F. The effective value of F must presumably allow for the dielectric constant of water!* In building up a theory of bodily transport for ordinary ions in water it is certainly only the electric *force* which is effective. The motion of the ion can be regarded as taking place in a needle shaped cavity cleared of polarizable material, and in such a cavity the effective force is the electric intensity corresponding to the volts/cm applied between the electrodes. But in discussing the transitions of §14 in which the ionic system as a whole does not move, it is clear that the effective force biassing the jumps, *a bias which is of the nature of a polarisation effect*, must by Lorentz's argument be taken to be the force at the centre of a spherical cavity round the system, for the symmetry of the distribution round the immobile system maintains the usual zero contribution from the matter inside the sphere. It follows easily from this that the effective value of $F$ in (16) must be taken to be

$$\tfrac{1}{3}(\eta+2)F^*/300,$$

where $F^*$ is given in volts/cm between the electrodes, $\eta$ being the dielectric constant of water. The factor 1/300 of course reduces volts to absolute electrostatic units.

(iii) *Values of the interaction integrals.* The value of this last factor in (16) is more difficult to estimate and can best be arrived at by first making calculations for a simple model. If we take a model in which each location is represented by a vertical sided hole of a constant depth ($U=0$ outside the hole, $U=-B$ within the hole), then without computing the wave functions we can see that roughly

$$\int\varphi\psi d\tau = 2\int_{\text{hole}}\varphi\psi d\tau$$

(actually this value is a lower limit),

$$-\int U(r_2)\varphi\psi d\tau = B\int_{\text{hole}}\varphi\psi d\tau,$$

while $\int U(r_2)\psi^2 d\tau$ is considerably smaller. Thus for this model

$$\frac{\int\varphi\psi d\tau}{-\int\varphi\psi U d\tau+(\int\varphi\psi d\tau)\int U(r_2)\psi^2 d\tau}=\frac{2}{B};\quad(23)$$

for any reasonably similar model we shall obtain a result of the same form if a suitable mean depth of the hole is used for $B$. It is important to observe that the ratio (23) does not depend on $R$ to any important extent. $R$ controls affairs not by affecting the distribution of the proton over the pair of water molecules but by affecting violently the rate of adjustment of the distribution, as we shall shortly verify.

(iv) *Conversion of (16) to three dimensions.* Eq. (22) refers to a one-dimensional world in which every jump is either up or down the field. In order to convert it to a three-dimensional world it is only necessary to recognise that situations will be offered for jumps to occur in every direction distributed at random. For directions making an angle $\theta$ with the applied field $\Delta$ becomes $\Delta\cos\theta$ and $F^*$, $F^*\cos\theta$. If then $N$ continues to denote the rate of presentation of occasions for jumps in any direction we must multiply (16) by $\overline{\cos^2\theta}$ or $\frac{1}{3}$ to make it apply to three dimensions. Another effect of converting to three dimensions is that in three dimensions the effect of a particular oxonium ion on the polarity of the water molecules does not necessarily extend indefinitely along a coordinated chain, but is broken up by the formation of rings. This favours the simple version of the theory here presented.

(v) *Values of R and B.* A pair of close water molecules are $2.8\times10^{-8}$ cm apart and in a free water molecule the protons are about $10^{-8}$ cm from the oxygen nucleus. The centres of the two

locations would therefore be about $0.8\times10^{-8}$ cm apart if there were no modification of the neutral $OH_2$. But there will be such modification, for the third proton will tend to increase the distances of all the protons from the centre and the polarisation of the molecules by the proton near their point of contact will tend still further to pull out the proton and to lower the barrier between the locations. The effective distance apart of the locations will therefore be smaller than $8\times10^{-9}$ cm and we shall take $6\times10^{-9}$ cm as a fair estimate.

It is not easy to estimate $B$ satisfactorily. The third proton is of course not bound so firmly as the second proton to $(OH)^-$ in forming neutral $OH_2$. But from the general magnitude of the energies involved it is clear that $B$ is of the order of 1 volt rather than 1/10 or 10 volts, and we shall take $B=0.75$, admitting that this may be considerably in error. Some preliminary calculations on the basis of the present theory confirm this guess of the order of magnitude.

If we now insert these numerical values we find

$$D=1.04\times10^{-15}\,NF^*. \tag{24}$$

We observe that this will reproduce the observed values for $(OH_3)^+$ if $N=2.5\times10^{12}$. The discussion of the value of $N$ presents difficulties.

(vi) *The value of N.* $N$ is the number of favourable configurations which the oxonium ion may be expected to enter into per second, each one offering to a proton a chance of jumping in some direction to a neighbouring molecule within the limitations imposed by the theory.

We should start by recalling that the calculations made here proceed on the assumption that the time during which a favourable configuration lasts is at the worst comparable with the time of transition of the proton to and fro between the two locations available to it. It is necessary, therefore, to estimate this time. For the model already used in (iii) of this section we have sufficiently nearly

$$\epsilon_- - \epsilon_+ = 2B\int_{\text{hole}} \varphi\psi\, d\tau.$$

For estimating numerical orders of magnitude this may be taken to be equal to

$$2Be^{-\kappa R'(-E_0)^{\frac{1}{2}}}, \tag{25}$$

$E_0$ ($<0$) being in this model the depth of the natural energy level below the energy zero outside the holes, and $R'$ the width of the *barrier*. If we take holes of a radius $10^{-9}$ cm then $E_0=\frac{1}{2}$ volt and $R'=4\times10^{-9}$ cm, approximately. From the time factors in (16) we see that the transition time $\tau$ is $\frac{1}{2}h/(\epsilon_- - \epsilon_+)$. Therefore

$$\tau \backsimeq (h/4B)e^{\kappa R'(-E_0)^{\frac{1}{2}}} = 1.3\times10^{-15}e^{7\times10^{8}(-E_0)^{\frac{1}{2}}}, \tag{26}$$

$$= 1.3\times10^{-15+3.05\times10^{8}(-E_0)^{\frac{1}{2}}}. \tag{27}$$

Inserting the value of $E_0$ for our model we obtain

$$\tau\sim6.5\times10^{-13}. \tag{28}$$

We observe at once that this is practically equal to $1/N$, $N$ having the value required by (24). We conclude that $\tau$ and $1/N$ are of the same order of magnitude. This enables us to carry the argument forward more precisely than we could by any quantitative *a priori* estimation of the actual value of $N$. For in fact we now see that the speed of the migration is so high that it is controlled by $\tau$ and not by $N$. The actual excess mobility is just of the order that one would expect *if the opportunities for jumping from one molecule to the next are infinitely frequent*, or more exactly, *are presented to the* $(OH_3)^+$ *ion at least as frequently as it can make use of them, the time required for any single jump being of the order* $\tau$. It only remains, therefore, to see whether this conclusion fits in with our conception of the structure of water.

## §16. The value of N, and the structure of water

Let us consider first of all what value of $N$ we should expect if water were a quasi-close packed structure of freely rotating molecules and ions. This is the most disordered arrangement that a liquid could possess and presumably it represents fairly closely the actual structure of say liquid argon and the actual structure that water would have, were it not that the molecules carry strong dipoles.

Such water molecules could be regarded with sufficient accuracy as classical isotropic rotators whose moment of inertia $I$ is about $2\times10^{-40}$g cm$^2$. Their average component of angular velocity, $\omega_x$ say, is given by

$$\tfrac{1}{2}I\omega_x^2 = \tfrac{1}{2}kT,$$

where $k$ is Boltzmann's constant. At ordinary temperatures, therefore, $\omega_x = 1.4 \times 10^{13}$ rad./sec., and the resultant $\omega$ is about $2.5 \times 10^{-13}$ rad./sec., a speed comparable with $1/\tau$. Now each $(OH_3)^+$ ion carries three protons and each $OH_2$ molecule at least one free location and in close packing there would be twelve closest neighbours round each ion. The locations, however, are fairly small and must be hit fairly accurately to be effective. In spite, therefore, of the large number of possible chances per rotation it is clear that a successful orientation as frequent as one per rotation is most unlikely.*

This conclusion fits in therefore most satisfactorily with the views here developed concerning the coordinated structure of water. In general the protons are permanently situated so that jumps from one $OH_2$ carrier to the next can occur at a rate of the order of $1/\tau$ times per second, just sufficient therefore to account for the abnormal mobility. The arguments given here for our isolated pair of molecules will apply at least roughly to any pair of molecules in a chain or other coordinated structure when an extra proton is present.

## §17. The hydroxyl ion

The extra mobility of the $(OH)^-$ is about one-half that of $(OH_3)^+$. It is obviously necessary and possible to accept the same general explanation for the extra mobility of both ions. It only remains to ask whether one can account theoretically for the fact that the extra mobility of $(OH_3)^+$ is greater than that of $(OH)^-$. It is clear that this follows from the theory for the two processes are: (1) A transfer of $H^+$ from $(OH_3)^+$ to $OH_2$. (2) A transfer of $H^+$ from $OH_2$ to $(OH)^-$. Now the proton levels in $(OH_3)^+$ will be slightly nearer the periphery of the molecule and perhaps be slightly less tightly bound than the proton levels in $OH_2$ owing to the repulsive effects of the extra proton. On referring to the formulae (22) and (26) for $D$ and $\tau$ we see that there are small changes probable in $R$ and $B$ which will hardly alter $D$ apart from the effect on $\tau$. But slight increases in $R$ and $-E_0$ will both increase $\tau$ and therefore diminish $N$; and this must be the dominant effect since it occurs in a moderately large exponent, and we must expect on the theory a lesser extra mobility for $(OH)^-$ just as is observed.

## §18. Temperature effects

We do not propose to attempt a discussion of the theoretical temperature coefficient of $D$ at this stage. We shall content ourselves at present with pointing out the general way in which temperature can come in. In the first place the only directly temperature dependent factor in the theory as it stands is $\eta$, the dielectric constant. $\eta$ falls as the temperature rises and so the extra mobility would *fall*. (We assume that the structure of the water continues to be sufficiently organized for plenty of opportunities for proton jumps.) The extra mobility is abnormal and does not increase so fast as the ordinary mobility which is controlled in effect by the viscosity of the water. But it apparently does increase and

* The number of favourable configurations per revolution can be roughly estimated by the following argument.

On one full rotation of the oxonium ion, any one of the protons it carries, $P$ in number, describe small circles of radii $\frac{1}{2}\Delta \sin\theta$ where $\theta$ is the angle that the proton's radius vector makes with the axis of rotation. The length of the path swept out, averaged for all axes of rotation, is therefore $\frac{1}{2}\pi\Delta$, $\Delta$ being as before the diameter of the ion. Round any ion there are $\chi$ closest neighbours and each of the $\chi$ lines of centres to these neighbours is a spot at which jumps might occur if a proton on the ion and an empty location on the molecule come simultaneously together there. The probability that on one rotation one of the protons comes within a small distance $\delta$ of one line of centres is the ratio of the area of the track of width $2\delta$ swept out by the proton to the area of the oxonium sphere, that is

$$(\tfrac{1}{2}\pi\Delta \cdot 2\delta)/\pi\Delta^2.$$

The average number of close approaches per revolution is therefore

$$\chi P\delta/\Delta.$$

Such a close approach can only be effective if an empty location is also present at the right moment. The chance that a location at a given moment will be within $\delta'$ of the line of centres is $\pi\delta'^2/\pi\Delta^2$. Combining the chance with the previous calculation, the average number of double close approaches per revolution is

$$\chi P\delta\delta'^2/\Delta^3.$$

This is, of course, only a rough estimate—calculations should strictly be made of the nature of those for *triple* gas collisions. But the order of magnitude should be correct for the number of intimate encounters per revolution in which transitions might occur. If we take $P=3$, $\chi=12$, $\delta=\delta'=2.5\times10^{-9}$, $\Delta=2.8\times10^{-8}$ cm then the number per revolution is 1/40.

not fall at ordinary temperatures as the temperature rises. This could only be explained on this simple version of the theory as due to a diminution of $\tau$ for a certain fraction of the protons. This might occur because some protons are thermally excited into upper states and so able to make more rapid transitions. Or again the thermal agitation might cause a fraction of the water molecule pairs to be unusually close together. We shall not discuss such points further here, for no such discussion would be of value when based on a more elaborate version taking account of the rate of thermal rearrangements of the coordinated chains referred to in §14. We have been concerned here rather to show that even for the largest likely values of $\tau$ the transitions can be rapid enough to produce the extra mobility in a suitable coordinated water. It may well be that the real $\tau$ is smaller and that the mobility is controlled partly by $\tau$ and partly by the thermal rearrangement rate so that the observed temperature effect may enter here.

## §19. The mobility of the isotope $H^2$

It is not intended that the preceding theory or the details of the model are to be relied upon too closely. In fact the details of the model on which the discussion of the mobility is based have been chosen rather unfavourably for the theory, so as to show that the quantum mechanical jumps must *at the worst* be capable of giving the extra mobility required, provided that there is a substantial amount of permanent coordination in the water structure. Provided, however, that the details are only approximately correct we can show that the effective mobility of the isotope ($H^2$) must be much less than that of the ordinary ($H^1$). The only important effect of the change of mass will occur in $\tau$. In $\tau$ we have $\kappa' = 2^{\frac{1}{2}}\kappa$ and also a slight increase in $-E_0$. This will change the second part of the index in (27) to $4.31 \times 10^6(-E_0')^{\frac{1}{2}}$ so that $\tau' \backsimeq 10^{-11}$, about 20 times greater. The extra mobility of ($H^2$) will therefore be about 20 times less than that of ($H^1$), and may therefore be neglected compared with the mobility by bodily transport even if the factor 20 is somewhat overestimated.

We conclude that the effective mobility of ($H^1$) is about 5 times that of ($H^2$) in aqueous solution. This conclusion may be of importance in the theory of the separation of the isotopes of hydrogen by electrolysis. It must not, however, be assumed that it is necessarily a dominant factor. Electrode processes which will also discriminate in favour of the more rapid removal of $H^1$ from the solution may be more important.

In concluding this paper at this point we must make some apology. It is clear that the ideas here developed, if they are at all correct, will lend themselves to a number of further applications along the same lines, particularly in physical and chemical applications of the hydrogen bond. But the recent success of G. N. Lewis and others in concentrating $H^2$ in bulk gives such great possibilities of new experiments in this field that it is undesirable to publish at this stage further uncontrolled speculations.

# X-Ray and Electron Diffraction of Iodine and the Diiodobenzenes

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The crystal structures of 1,3 and 1,4 diiodobenzene were determined from the x-ray diffraction patterns of single crystals. The separations of the iodine atoms in the molecules were found to be 6.85 and 5.92A, respectively. These values are in agreement with results obtained by analysis of the electron diffraction patterns given by the vapors of these compounds. The most satisfactory explanation of the electron diffraction results for 1,2 diiodobenzene requires the I−C valence directions to be bent by about 10° from symmetrical positions in the plane of the benzene ring. In this molecule the I−I distance was found to be 4.00A, which is approximately the same as the minimum intermolecular iodine distances in crystals of the other isomeric diiodobenzenes. Electron diffraction was obtained from vapors of carbon tetrachloride and iodine. The separation of the iodine atoms in the latter molecule was found to be 2.64A; a value in agreement with band spectra data and with previous crystal structure analysis.

COHERENT scattering of electrons and x-rays are utilized in the present work for determining the atomic configurations of iodine and the three isomeric diiodobenzenes. Analyses of x-ray diffraction patterns of crystalline 1,3 and 1,4 diiodobenzene readily led to the allocation of the iodine atoms in the units of structure and to knowledge of the molecular orientations. Diffraction of electrons from vapors of these compounds and from 1,2 diiodobenzene and iodine permitted determinations of iodine to iodine distances within the molecules.[1]

## ELECTRON DIFFRACTION

### Theory

The angular distribution of electrons elastically scattered from a molecular vapor can be explained by use of the Debye interference formula[2] developed for coherent scattering of x-rays from polyatomic molecules together with the theory of Mott[3] and Bethe[4] for elastic scattering of electrons by monatomic gases. The formulas of Mott and Bethe have been found to agree approximately with results of experiments[5] provided that the electron velocities are sufficient so that the effect of atomic polarizations and electron interchanges will be unimportant. These theories are contained in the following formula[6] for $I(\theta)$, a quantity that is directly proportional to the number of electrons scattered elastically, at an angle $\theta$, per unit solid angle per unit intensity of the primary beam.

$$I(\theta) = \sum_{i=1}^{n} \sum_{j=1}^{m} \psi_i \psi_j (\sin x_{ij}/x_{ij}) \qquad (1)$$

[1] *Preparation of compounds.* We are indebted to Mr. E. F. Jansen of this laboratory for the preparation of 1,2 diiodobenzene. 1,2 iodonitrobenzene was made by the diazotization of 1,2 nitroaniline followed by treatment with KI (Busch and Walbring, J. prakt. Chem. (2) **71**, 374 (1905)). The reduction of this compound to 1,2 iodoaniline was effected by treatment with $SnCl_2$ in acetic acid solution. (Thiele, Ann. d. Chemie **305**, 114 (1899)). Diazotized 1,2 iodoaniline reacts explosively with KI to form 1,2 diiodobenzene (m. p. 26°). 1,3 diiodobenzene was prepared by the tetra-azotization of *m*-phenylenediamine followed by treatment with KI (cold). It was separated by steam distillation, extracted with ether, dried, and distilled (m. p. 39°). 1,4 diiodobenzene was purchased from the Eastman Company.

[2] P. Debye, Ann. d. Physik **46**, 809 (1915).

[3] N. F. Mott, Proc. Camb. Soc. **25**, 304 (1929); Proc. Roy. Soc. **A127**, 658 (1930).

[4] H. Bethe, Ann. d. Physik **87**, 55 (1928); ibid. **5**, 325 (1930).

[5] For the extent of experimental confirmation of the theory of Mott and Bethe see: N. F. Mott, reference 3; H. Mark and R. Wierl, Zeits. f. Physik **60**, 741 (1930); F. L. Arnot, Proc. Roy. Soc. **A133**, 615 (1931); A. L. Hughes and J. R. McMillen, Phys. Rev. **39**, 585 (1932); John T. Tate and R. Ronald Palmer, Phys. Rev. **40**, 731 (1932); A. L. Hughes, J. H. McMillen and G. M. Webb, Phys. Rev. **41**, 154 (1932); A. L. Hughes, Phys. Rev. **42**, 147 (1932).

[6] See R. Wierl, Ann. d. Physik **8**, 521 (1931).

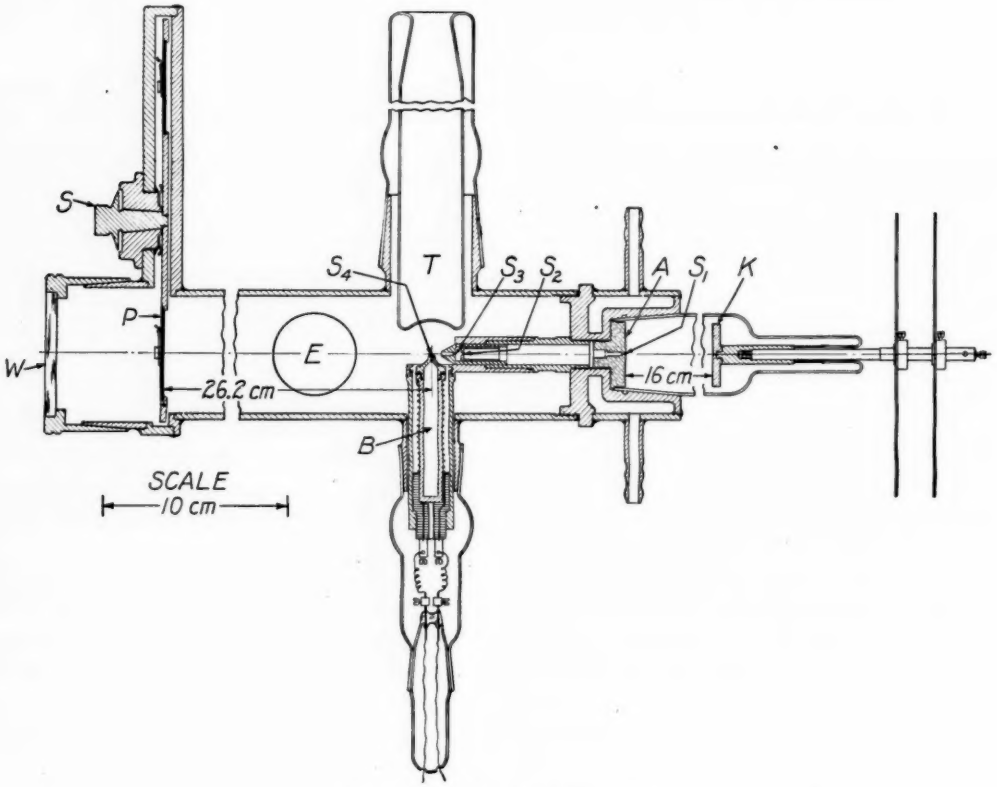



FIG. 1. Diagram of the apparatus.

where

$$x_{ij}=4\pi l_{ij}[(\sin\theta/2)/\lambda] \quad (2)$$

$$\psi_{ij}=(Z_i-F_i)/[(\sin\theta/2)/\lambda]^2. \quad (3)$$

In these expressions $l_{ij}$ is the distance between the $i$th and the $j$th atom, $\lambda$ is the de Broglie wave-length of the electrons, and $Z_i$ and $F_i$ are the atomic number and atomic scattering factor of the $i$th atom, respectively.

**Experimental arrangement**

The apparatus used, a modification of that described by Wierl,[6] is diagrammatically shown in Fig. 1. Electrons originating from the cold cathode $K$ of a gas discharge tube were limited to a fine beam by a tube $S_1$ 0.2 mm in diameter and 2 mm long and by two holes $S_2$ and $S_3$ each 0.1 mm in diameter. The electrons, after penetrating the molecular beam formed by the vapor coming from the nozzle $S_4$, were finally recorded on the photographic plate $P$. Vapors issuing from the nozzle, which was about 0.3 mm in diameter and 5 mm long, were condensed on the liquid air trap $T$. The pressure in the boiler $B$ was usually about 10 mm Hg, while a pressure of less than $10^{-3}$ mm Hg was maintained in the diffraction chamber. This was obtained by rapid pumping at $E$ with a three-stage Gaede steel pump supported by a Cenco megavac pump.

Eastman lantern slide plates were used for recording the diffraction patterns. They were mounted at $P$ in sectors of a disk that could be rotated by means of the cone $S$ so that five consecutive exposures could be taken. The diffraction pattern appearing on a fluorescent screen placed in one of the sectors could be observed through the clear glass window $W$.

This discharge tube was operated with constant d.c. potential supplied by a filter circuit similar to that described by Hull.[7] The primary excitation of the high voltage transformer was supplied by a 60-cycle a.c. generator driven by a synchronous motor. Two Meirowsky condensers connected in parallel, having a total capacity of

[7] A. W. Hull, Gen. Elec. Rev. **19**, 173 (1916).

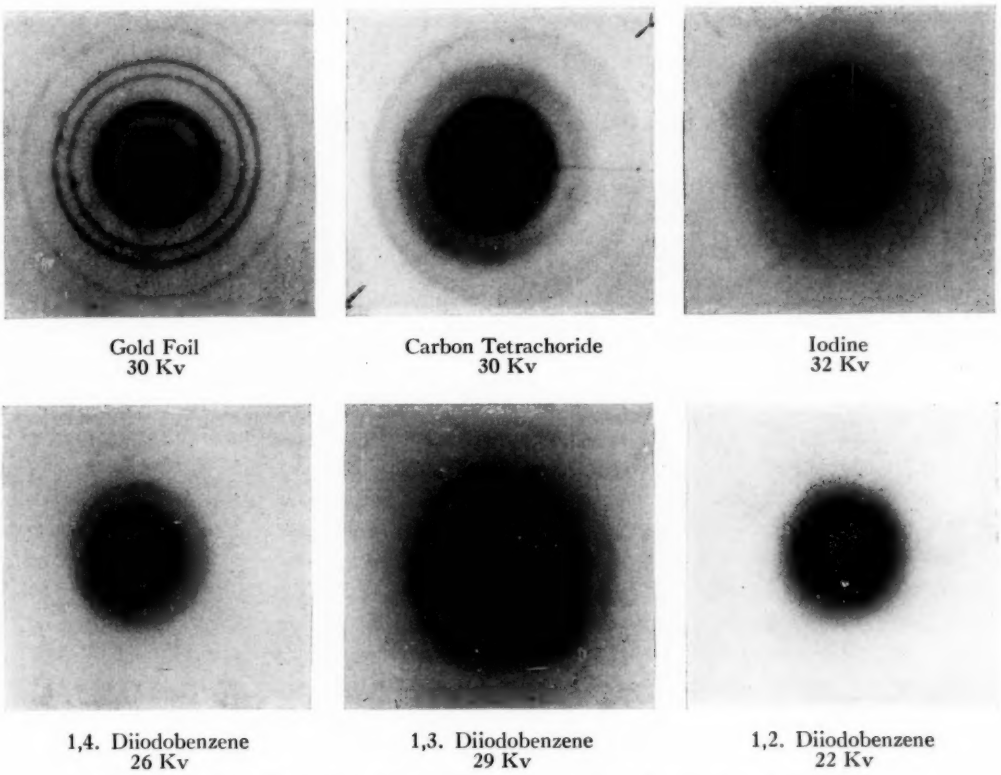



FIG. 2. Electron diffraction photographs, exposure times 3 seconds to 2 minutes.

0.2 microfarad, were used for maintaining a constant voltage together with an inductance of about 2000 henries. The potential across the discharge tube, 40 kv maximum, was measured by a static voltmeter according to the design developed by W. W. Nicholas.[8] The voltmeter was calibrated by the use of electron diffraction patterns obtained from a thin gold foil. These results were compared with voltage measurements made by means of Taylor high voltage resistances.[9] After including a small relativity correction, it was found that the two methods of determining the de Broglie wave-lengths of the electrons were in agreement to within about one percent.

## Experimental results

*Carbon tetrachloride.* The densitometer record of an electron diffraction photograph, reproduced in Fig. 2, given by carbon tetrachloride vapor is shown in Fig. 3. A true interference maximum is obtained that is in better agreement with the theoretical intensity curve[10] than has been reported heretofore for the case of electron diffraction. In this particular instance the compound was placed in a glass container connected through a stopcock to the jet shown at $S_4$, Fig. 1.

Values of $(1/\lambda)\sin\theta/2$ for the first three maxima as measured by various observers are listed in Table I. The values obtained by Wierl, Hengstenberg and Brú[11] and by the writers are in

TABLE I. *Comparison of electron diffraction values of* $(\sin\theta/2)/\lambda$ *for carbon tetrachloride.*

| Maximum | Wierl | Brockway & Pauling | Hengstenberg & Brú | Present work |
|---|---|---|---|---|
| 1 | 0.197 | 0.212; 0.220 | Agreement with | 0.197±0.003 |
| 2 | .364 | .376; .385 | Wierl to | .364± .003 |
| 3 | .543 | .558; .569 | within ½% | .548± .005 |

[8] W. W. Nicholas, Bur. Standards J. Research **8**, 111 (1932).

[9] We are indebted to Dr. L. S. Taylor of the United States Bureau of Standards, for the loan of the resistances used.

[10] For theoretical intensity curve for $CCl_4$ see R. Wierl, reference 6.

[11] J. Hengstenberg and L. Brú, Anales Soc. Espana. Fis y Quim. **30**, 341 (1932).

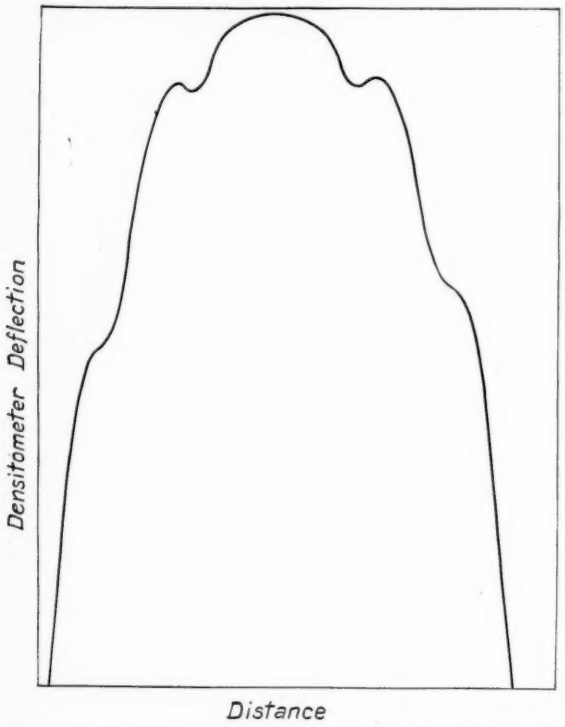



FIG. 3. Densitometer record for electron diffraction of $CCl_4$.

good agreement. The Cl−Cl distance for the tetrahedral molecule calculated from these data is 2.98A. The results of Brockway and Pauling[12] differ appreciably from those obtained by other observers. Our values for the first two maxima are averages obtained from eight photographs at various voltages, exposure times and molecular beam concentrations. The third maximum was measured on only two plates.

*Iodine.* The theoretical scattering curve for iodine is obtained from Eq. (1) which reduces to

$$I(\theta) = 2\psi_I\psi_I(1+\sin x/x) \qquad (4)$$

where $\psi_I = (Z_I - F_I)/((\sin\theta/2)/\lambda)^2$. Fig. 4 shows $I(\theta)$ plotted as a function of $x$ and of $(1/\lambda)\sin\theta/2$. The I−I distance was assumed to be 2.66A as found from band spectra data[13] and in this instance as well as in the case of subsequent molecules the values of $F_i$ used were obtained from Pauling's and Sherman's[14] calculations for electron distributions corresponding to Schrödinger eigenfunctions for hydrogen-like atoms.

[12] L. A. Brockway and Linus Pauling, Proc. Nat. Acad. Sci. **19**, 68 (1933).

The apparent diffraction rings do not correspond to true maxima but rather to points of inflection (note Fig. 4). Their diameters depend upon $\psi_I$ which is a function of the atomic separation, the quantity to be measured. Fortunately small changes in $l_{ij}$ do not greatly affect the maxima or inflection points expressed as a function of $x_{ij}$. This justifies the use of approximate values of $l$ in computing the intensity curve.

The experimental results are given in Table II.

TABLE II. *Electron diffraction results for iodine.*

| Plate No. | Wave-length in A | $(\sin\theta/2)/\lambda$ 1st Maximum | 2nd Maximum |
|---|---|---|---|
| 1 | 0.0638 | 0.223 | 0.403 |
| 2 | .0648 | .224 | .402 |
| 3 | .0667 | .236 | .415 |
| 4 | .0667 | .222 | .402 |
| 5 | .0667 | .222 | .402 |
| 6 | .0667 | .222 | .408 |
| 7 | .0695 | .226 | |
| 8 | .0695 | .226 | |
| 9 | .0748 | .239 | |
| Average values | | 0.226±0.002 | 0.405±0.002 |

I−I = 2.64±0.15A; 2.65±0.10A

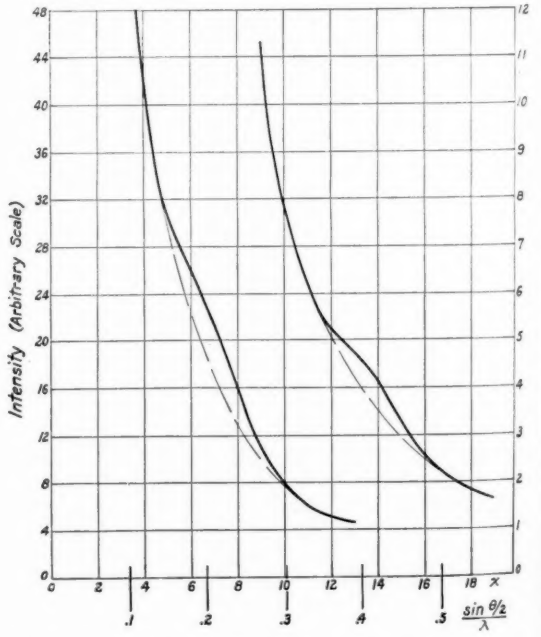



FIG. 4. Theoretical electron diffraction curve for iodine.

[13] R. T. Birge, Int. Crit. Tab. **5**, 409 (1929).

[14] L. Pauling and J. Sherman, Zeits. f. Kristallographie **81**, 1 (1932).

The average values obtained for $(1/\lambda)\sin\theta/2$ are 0.226 and 0.405 for the first and second diffraction rings, respectively. The theoretical values of $x$ corresponding to these rings are 7.5 and 13.5 as seen from Fig. 4. From Eq. (2) we obtain 2.64A and 2.65A as the I−I distance.

*1,4 diiodobenzene.* The chief interest in the analyses of the diiodobenzenes lies in the determination of the I−I distances. The iodine atoms produce the majority of the scattering, and consequently afford a method for measuring the I−I separations. However, the scattering from the other atoms cannot be neglected for although the scattering produced by them is small it is also a very irregular function of $(\theta)$ and when superimposed upon the iodine-iodine scattering may give maxima or minima of importance.

In general the procedure adopted has been to calculate a complete scattering curve for a molecular model based upon prior information. The positions of the maxima or prominences are then compared and in case of poor agreement the calculations are repeated for a somewhat different model. This procedure is followed until good agreement is obtained. The solution, although not unique, is sufficient and in the case of the diiodobenzenes undoubtedly gives the separation of the iodine atoms and confirms the geometry of the molecules.

The assumed structure of 1,4 diiodobenzene is shown in Fig. 5. The C−C distance of 1.42A is the value obtained from x-ray measurements on hexamethyl benzene[15] and from electron diffraction data of benzene vapor.[6] The value of 1.12A for the C−H distance was obtained from band spectra data on CH[16] while the I−C separation, 2.10A, was obtained as an extrapolation of the Cl−C and Br−C distances in a number of organic compounds.[17]

On applying Eq. (1) we can evaluate $I(\theta)$ for 1,4 diiodobenzene as follows

$$I(\theta)=I_{II}+I_{IC}+I_{CC}+I_{IH}+I_{HC}+I_{HH} \tag{5}$$

where $I_{nm}$ is the intensity of coherent scattering between atoms of type $n$ and $m$. The $\psi_i\psi_j$ factors are important in determining the relative magnitudes of the various terms in Eq. (5). The terms $I_{HC}$ and $I_{HH}$ can be shown to be negligibly small while the contribution of $I_{IH}$ is small and in most instances can be omitted although it should be included for an accurate analysis. If the distances assumed above are used Eq. (5) reduces to

$$I_{II}=2\psi_I\psi_I(1+\sin 4.95x_{cc}/4.95x_{cc}), \tag{6}$$

$$I_{IC}=4\psi_c\psi_I\left[\frac{\sin 1.48x_{cc}}{1.48x_{cc}}+2\frac{\sin 2.14x_{cc}}{2.14x_{cc}}+2\frac{\sin 3.1x_{cc}}{3.1x_{cc}}+\frac{\sin 3.48x_{cc}}{3.48x_{cc}}\right], \tag{7}$$

$$I_{cc}=6\psi_c\psi_c[1+2\sin x_{cc}/x_{cc}+\sin 2x_{cc}/2x_{cc}+2\sin 3\tfrac{1}{2}x_{cc}/3\tfrac{1}{2}x_{cc}], \tag{8}$$

$$I_{IH}=8\psi_I\psi_H[\sin 2.2x_{cc}/2.2x_{cc}+\sin 3.70x_{cc}/3.70x_{cc}], \tag{9}$$

where

$$x_{cc}=4\pi l_{cc}(\sin\theta/2)/\lambda=x_{II}/4.95, \tag{10}$$

$l_{cc}$ = C−C distance = 1.42A.

The complete intensity curve is shown in Fig. 5. In order to determine the dependence of the position of the diffraction rings on the I−C distance similar curves were calculated for values of $l_{IC}=1.90$A and 2.30A.

The experimental results are summarized in Table III. Values of $x_{cc}$ listed in this table are indicated in Fig. 5 by the arrows *a*, *b* and *c* for comparison with the calculated maxima which are indicated by smaller arrows. A photometer record of a typical plate, No. 15, is shown in Fig. 6. It is to be noted that this record gives a curve of approximately the type required by theory. The second maxima, (*b*), was used for the analysis since it could be measured with the greatest accuracy. Its mean position is between

[15] K. Lonsdale, Proc. Roy. Soc. (London) **A123**, 494 (1929).

[16] R. S. Mulliken, Rev. Mod. Phys. **4**, 83 (1932).

[17] S. B. Hendricks, Chem. Rev. **7**, 431 (1930).

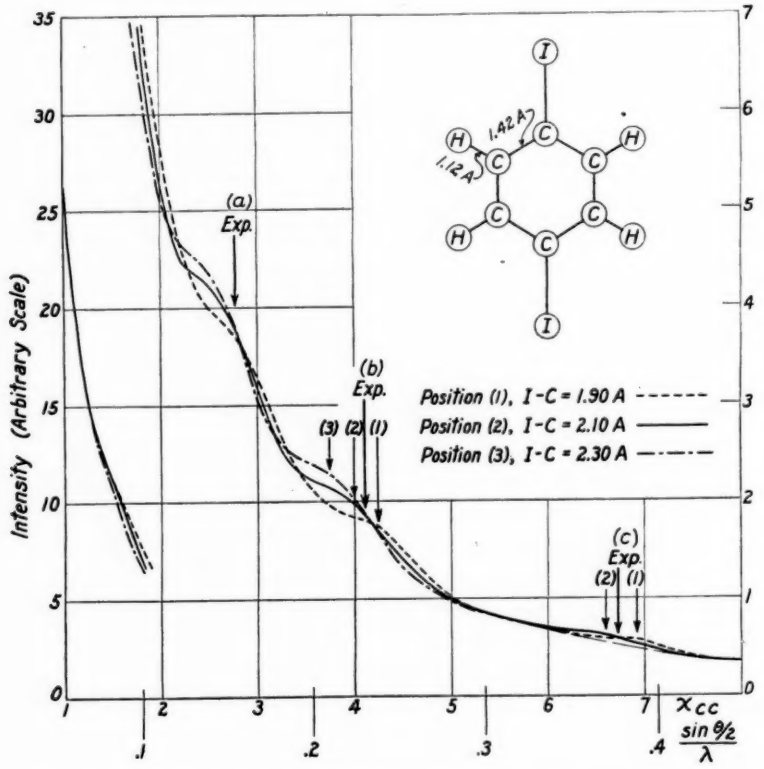



FIG. 5. Theoretical electron diffraction curves for 1,4 diiodobenzene. The arrows (a), (b) and (c) show the average positions of the observed diffraction rings in relation to the prominences on the theoretical curve. Similar comparisons are made in Figs. 7, 9 and 10.

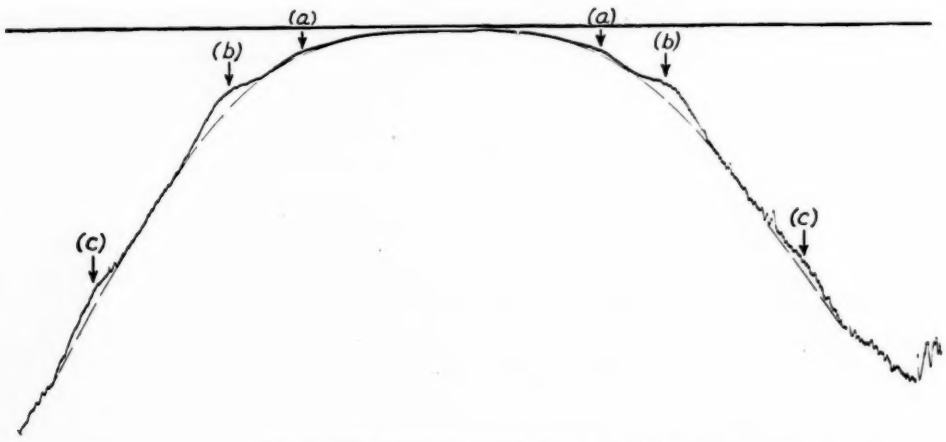



FIG. 6. Densitometer record for 1,4 diiodobenzene.

TABLE III. *Electron diffraction results for 1,4 diiodobenzene.*

| Plate No. | Wave-length in A | $(\sin\theta/2)/\lambda$ (a) 1st Maximum | (b) 2nd Maximum | (c) 3rd Maximum |
|---|---|---|---|---|
| 1 | 0.0626 | 0.161 | 0.226 | 0.370 |
| 2 | .0641 | .161 | .235 | .376 |
| 3 | .0648 | .162 | .236 | .382 |
| 4 | .065 | .151 | .226 | |
| 5 | .0653 | .156 | .236 | .380 |
| 6 | .0672 | .157 | .230 | .378 |
| 7 | .069 | .156 | .230 | |
| 8 | .074 | .152 | .226 | present |
| 9 | .074 | .154 | .222 | |
| 10 | .075 | .146 | .226 | |
| 11 | .0778 | .157 | .223 | |
| 12 | .0879 | .158 | .239 | .380 |
| 13 | .0883 | .162 | .239 | .380 |
| 14 | .0903 | .164 | .232 | .377 |
| 15 | .0960 | .151 | .223 | present |
| Average values | | 0.156 | 0.230 | 0.378 |
| $x_{cc}$ | | 2.78 | 4.10 | 6.75 |

I−I = 6.85±10A; I−C = 2.00A

TABLE IV. *Electron diffraction results for 1,3 diiodobenzene.*

| Plate No. | Wave-length in A | $(\sin\theta/2)/\lambda$ (a) 1st Maximum | (b) 2nd Maximum | (c) 3rd Maximum |
|---|---|---|---|---|
| 1 | 0.0620 | 0.185 | 0.268 | 0.352 |
| 2 | .0623 | .185 | | .351 |
| 3 | .0662 | .187 | | .359 |
| 4 | .0664 | .188 | .276 | .361 |
| 5 | .0665 | | | .359 |
| 6 | .0666 | | | .356 |
| 7 | .0667 | | | .360 |
| 8 | .0715 | .187 | | .360 |
| 9 | .0717 | .189 | | .358 |
| 10 | .0720 | | | .358 |
| 11 | .0720 | | | .358 |
| Average values | | 0.186 | 0.272 | 0.357 |
| $x_{cc}$ | | 3.32 | 4.85 | 6.37 |

I−I = 5.97±0.10A; I−C = 2.00A

the corresponding points on the curves calculated for I−C distances of 1.90A and 2.10A. Interpolation shows that the most probable I−C distance is 2.00A which gives an I−I separation of 6.85±0.10A.

Several photographs in which the rings *a*, *b* and *c* were very intense showed faint halos at $(1/\lambda)\sin\theta/2$ equal to about 0.3 and 0.45. The theoretical curve does not have corresponding points of inflection. Such a slight discrepancy is not unexpected in view of the approximations used in the theory.

*1,3 diiodobenzene.* Formulas for computing the scattering from this molecule are of the same form as for 1,4 diiodobenzene. Numerical quantities are changed, however, and the $I_{IH}$ term becomes

$$I_{IH} = 4\psi_I\psi_H\left[\frac{2\sin 2.2x_{cc}}{2.2x_{cc}} + \frac{\sin 4.26x_{cc}}{4.26x_{cc}} + \frac{\sin 3.7x_{cc}}{3.7x_{cc}}\right]. \tag{11}$$

A complete intensity curve was calculated for an I−C distance of 1.90A and a partial curve for 2.10A in the region including the third and most pronounced maxima as shown in Fig. 7. A densitometer record with prominences (*b*) and (*c*) quite apparent may be seen in Fig. 8. (*c*) is the prominent ring noticeable in Fig. 2. It was used for determining the positions of the iodine atoms.

The experimental results are summarized in Table IV. The mean values obtained for $x_{cc}$ are indicated in Fig. 7. The position of the third maxima lies between the maxima on the curves calculated for I−C distances of 1.90A and 2.10A. Interpolation gives 2.03A as the best value for this distance, the corresponding I−I distance being 5.97±0.10A.

*1,2 diiodobenzene.* Experimental results obtained from this compound are shown in Table V. A typical densitometer record is reproduced in Fig. 11. The most prominent ring appears at $x_{cc}=2.73$ with two other rings apparent at $x_{cc}=4.65$ and $x_{cc}=6.55$ on the photographs.

Values of $I(\theta)$ were calculated by the above methods for a model in which the I−C distances were assumed to be 2.10A and the I−C directions symmetrically placed with respect to the benzene ring, thus making the I−I separation 3.52A. The arrows (*a*), (*b*), and (*c*) on Fig. 9 show the location of the experimentally observed rings;

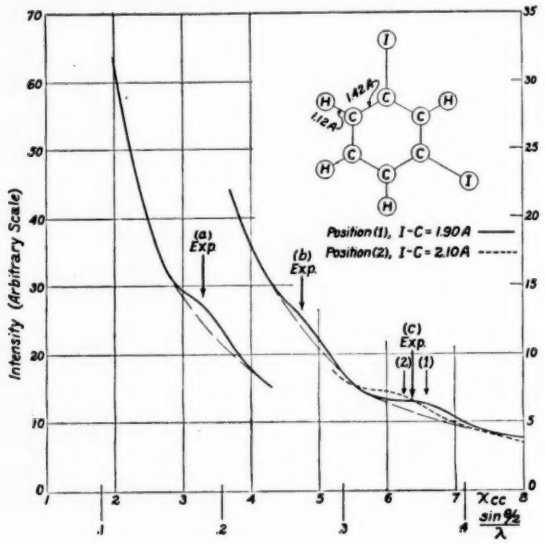



FIG. 7. Theoretical electron diffraction curves for 1,3 diiodobenzene.

TABLE V. *Electron diffraction results for 1,2 diiodobenzene.*

| Plate No. | Wave-length in A | (sin θ/2)/λ 1st Maximum | 2nd Maximum | 3rd Maximum |
|---|---|---|---|---|
| 1 | 0.0639 | 0.157 | 0.261 | |
| 2 | .0642 | .148 | .252 | |
| 3 | .0648 | .149 | .265 | |
| 4 | .0648 | .154 | .265 | |
| 5 | .0648 | .151 | .279 | 0.368 |
| 6 | .0648 | .151 | | |
| 7 | .0649 | .150 | .264 | |
| 8 | .0650 | .151 | .249 | |
| 9 | .065 | .151 | | |
| 10 | .0797 | .156 | .258 | |
| 11 | .0797 | .156 | .252 | |
| 12 | .0805 | .154 | .261 | .366 |
| 13 | .0805 | .154 | .261 | .368 |
| 14 | .0810 | .153 | | |
| Average values | | 0.153 | 0.261 | 0.367 |
| | $x_{cc}$ | 2.73 | 4.65 | 6.55 |

I−I=4.00±0.10A; I−C=2.00±0.10A

these are to be compared with the calculated prominences. Although the first diffraction ring is in good agreement with the experiment, the theoretical curve does not account for the observed rings (*b*) and (*c*).

A theoretical scattering curve was calculated for this molecule in which the I−C distance was increased to 2.60A thus making the I−I separation 4.00A. The second and third maxima predicted by this curve were again out of agreement with the positions of the observed diffraction rings, whereas the position of the first maxima corresponded approximately with the first experimental ring observed. The lack of agreement between the results and the theory for these two cases justifies the elimination of these models as possible representations of the structure of 1,2 diiodobenzene.

Calculations made for a third model in which the I−C distance was assumed to be 2.00A and the I−I distance to be 4.00A are illustrated in Fig. 10. This corresponds to a change in the I−C direction of about 10° from the former case and leaves a resultant unsymmetrical molecule. The curve shows three regions of inflection points agreeing approximately with the experimentally observed rings. The agreement is, however, not as good as obtained in the compounds previously

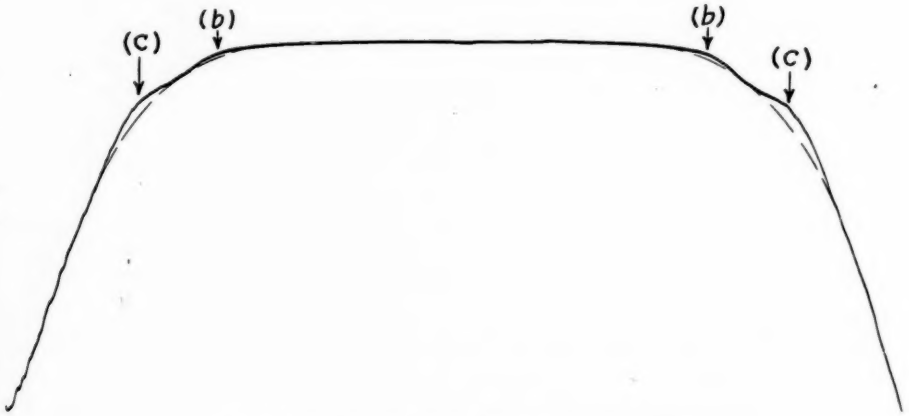



FIG. 8. Densitometer record for 1,3 diiodobenzene.

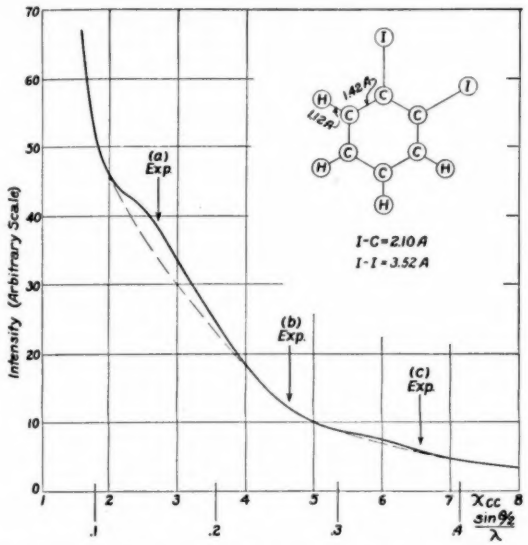



FIG. 9. Theoretical electron diffraction curve for 1,2 diiodobenzene with I−C=2.10A and I−I=3.52A.

discussed. The theoretical position of the first maxima is somewhat closer to the origin than is the observed ring. We conclude, however, that the atomic arrangement approximates that shown in Fig. 10.

## X-RAY DIFFRACTION

Analysis of x-ray diffraction patterns from crystalline 1,4 and 1,3 diiodobenzene led to

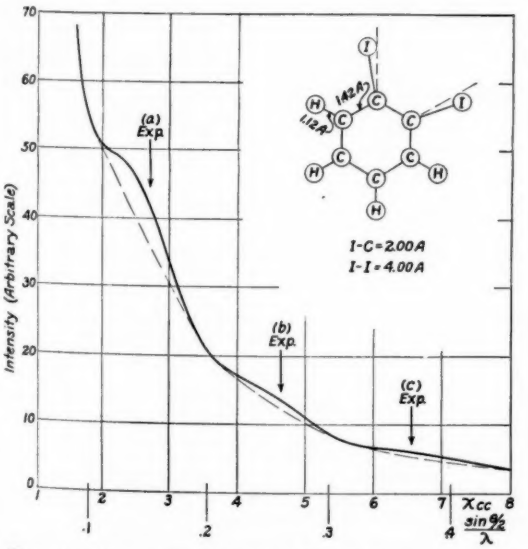



FIG. 10. Theoretical electron diffraction curve for 1,2 diiodobenzene with I−C=2.00A and the valence direction bent by approximately 10° to give I−I=4.00A.

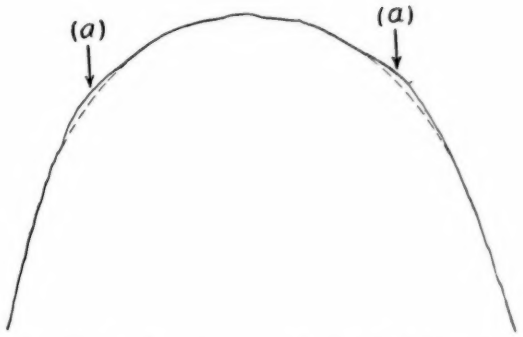



FIG. 11. Densitometer record for 1,2 diiodobenzene.

independent determinations of the molecular structures. The intensity of x-radiation coherently scattered at a particular angle by a free atom is a function of $F^2$ rather than of $(Z-F)^2$ as for electron diffraction. The probability for scattering by an iodine atom relative to a carbon atom, for values of $(1/\lambda)\sin\theta/2$ greater than 0.2, is considerably enhanced for x-rays, as compared with electrons; thus, for example, with $(1/\lambda)\sin\theta/2$ equal to 0.3 the ratios are: $(Z-F)^2_I/(Z-F)^2_C=26$ and $F^2_I/F^2_C=207$. In the case of x-ray diffraction from a crystalline diiodobenzene the absolute intensities of the interference maxima will consequently be determined by the arrangement of the iodine atoms. The carbon atoms also can be expected to contribute partially out of phase to all reflections and thus further decrease their contributions to the amplitudes of the scattered waves. For these reasons the scattering from the carbon atoms has been neglected in the crystal structure determinations.

The relative intensities of "reflection" were qualitatively determined by visual comparison. Reflections from a number of planes were either absent or very weak in intensity. These data were first considered in the limitation of the parameters. The final restriction was obtained by comparing the values of $S/64\ F^2_I$ for various planes where $S=(F_IS')^2$, $S'$ being the structure amplitude.

On inspecting Tables VII–IX it should be borne in mind that the maximum value of $S/64\ F^2_I$ is 1.0 and that $F_I$ is a function of $\theta$, i.e., a variable from plane to plane that decreases with increase in $\theta$. The parameters were determined by considering the various intensities of reflection in

the orders given. The usual graphical methods of presenting these essential data would be too detailed for inclusion here.

**Experimental methods**

Crystals of 1,4 diiodobenzene were grown by cooling saturated solutions in absolute alcohol; those of the 1,2 compound, by crystallization at constant temperature from supersaturated solutions. Crystals of 1,3 diiodobenzene were prepared by sublimation. The densities, where unknown, were determined by suspension in Rohrbach's solution in glycerine.

Weissenberg, rotating crystal, and oscillating crystal photographs were made with Cu $K$ and Mo $K\alpha$ radiations. It was necessary, on account of the thinness of the crystals, to use Laue photographs from 1,3 diiodobenzene. These were produced with radiation from a tube with a tungsten anticathode operated at 26,000 $V$ peak (minimum $n\lambda = 0.48$A).

One lattice dimension, usually that of the prominently developed face, was measured accurately against $\beta$ $Al_2O_3$ as a reference ($d_{0001} = 22.480$A). Cu $K$ radiation was used in order to reduce the transmission of the crystals and thus to enhance the accuracy of the measurements. The other two dimensions were checked approximately from layer line separations and then calculated from the axial ratios. The crystallographic properties as listed by P. Groth[18] are summarized in Table VI.

TABLE VI. *Crystallographic properties of the diiodobenzenes.*

| Substance | m.p. | Crystal system and axial ratio (Groth) | Density obs. | Density calc. | Cleavage |
|---|---|---|---|---|---|
| 1,2 diiodo-benzene | 27.0 | Mon. Pris. $=93°56'$ $a:b:c=1.0489:1:1.5466$ | $2.73_{10°}$ | 2.72 | 11 to (010) |
| 1,3 diiodo-benzene | 40.4 | Rhom. Bipyramidal $a:b:c=1.1399:1:2.7704$ | 2.80 | 2.88 | 11 to (100) |
| 1,4 diiodo-benzene | 129.4 | Rhom. Bipyramidal $a:b:c=0.4342:1:0.3653$ | 2.79 | 2.79 | none |

*1,4 diiodobenzene.* $C_6H_4I_2$

| | |
|---|---|
| Orthorhombic bipyramidal | $4C_6H_4I_2$ in unit of structure |
| Lattice dimensions | Types of absences |
| $a = 17.00_4$ | $(0kl)$, $k$ odd |
| $b = 7.38_1$ | $(h0l)$, $l$ odd |
| $c = 6.21_0$ | $(hk0)$, $h$ odd |

Space Group $P\,m\,m\,m$, $P\,m\,c\,m$, $P\,m\,a\,b$, $P\,c\,a\,b$

[18] P. Groth, *Chemische Krystallographie*, Vol. IV, Leipzig (1917).

Over twenty-five planes of each type given above in positions to reflect were observed to be absent. The observed intensities of reflection were satisfactorily accounted for by an atomic arrangement derived from space group $P\,c\,a\,b - V_h^{15}$. Each molecule must have at least a center of symmetry.

*Atomic arrangement and parameter determinations.* The possible atomic positions are:[19]

$$xyz;\ x+\tfrac{1}{2},\ \tfrac{1}{2}-y,\ \bar{z};\ \bar{x},\ y+\tfrac{1}{2},\ \tfrac{1}{2}-z;\ \tfrac{1}{2}-x,\ \bar{y},\ z+\tfrac{1}{2}$$
$$\bar{x}\bar{y}\bar{z};\ \tfrac{1}{2}-x,\ y+\tfrac{1}{2},z;\ x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z;\ x+\tfrac{1}{2},\ y,\ \tfrac{1}{2}-z. \quad \text{(a)}$$

The molecular centers are at (b) or (c).

$$000;\ \tfrac{1}{2}\ \tfrac{1}{2}\ 0;\ 0\ \tfrac{1}{2}\ \tfrac{1}{2};\ \tfrac{1}{2}\ 0\ \tfrac{1}{2}, \quad \text{(b)}$$

$$\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2},\ 00\ \tfrac{1}{2};\ \tfrac{1}{2}\ 00;\ 0\ \tfrac{1}{2}\ 0. \quad \text{(c)}$$

The three separable parameters defining the positions of the iodine atoms are determined below.

(1) The observed intensities of $(h00)$, note (16.0.0)a., (11.0.2)m.w. (702)m. and (902)a. requires

$$x = 0.172 \pm 0.002.$$

(2) The observation that $(h20)$ and $(h00)$ have approximately the same intensities of reflection and that both (022) and (002) are v.s. requires $\cos 2\pi(2y)$ to have near its maximum value. The orders of intensities of $(h00)$, $(h10)$, $(h20)$, $(h30)$ requires $\sin 2\pi(y)$ and $\sin 2\pi(3y)$ to have near their maximum values but with $\sin 2\pi(3y)$ somewhat the greater. Finally $(043) > (023)$, (060) and (080) absent with (040) m.w., (250) m.s., and (450)m. requires

$$y = 0.40 \pm 0.01.$$

(3) The observations $(024) > (023)$; $(041) > (042)$; $(043) > (042)$, (004)m.s., (006)w., the observed intensities of $(h00)$ and $(h02)$, and (023) m.w., (025)v.w., (043)m., (045)w. requires

$$z = 0.22 \pm 0.01.$$

An inspection of Table VII will perhaps serve to show the concordance between observed intensities and calculated structure factors.

The positions of the iodine atoms in the

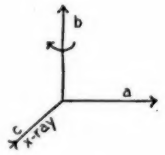
[19] See P. Niggli, *Geometrische Kristallographie des Diskontinuums*, p. 201, Leipzig (1919).

structure are shown in Fig. 12. There are as many possible positions for the molecules as there are symmetry centers in the crystals. Only one of these positions can be considered as probable however if the crystals are holohedral, namely $A-I$ as shown. The indicated positions of the carbon atoms are ones giving an intermolecular separation of ca 3.70A. The cleavages and optical properties of the crystals are satisfactorily accounted for.

TABLE VII. *Intensities of reflections, estimated, and structure factors, calculated for iodine atoms alone, for some planes of 1,4 diiodobenzene.*

Mo $K$ radiation, 30°–45° oscillation of the crystal.

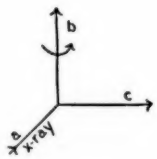
(1) ($hk0$) with $h$ odd required to be absent




| Equatorial zone | | | 1st layer line | | | 2nd layer line | | | 3rd layer line | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ |
| (200) | m. | 0.22 | | | 0.04 | | | | | | |
| (400) | m. | .14 | (410) | w. | .06 | | | | (430) | m.w. | 0.45 |
| (600) | v.s. | .96 | (610) | a. | .00 | (620) | m.s. | 0.73 | (630) | a. | .02 |
| (800) | s. | .51 | (810) | w. | .03 | (820) | m.s. | .39 | (830) | m.w. | .24 |
| (10.0.0) | v.w. | .04 | (10.1.0) | w. | .06 | (10.2.0) | v.w. | .03 | (10.3.0) | m.w. | .45 |
| (12.0.0) | m.s. | .85 | (12.1.0) | a. | .02 | (12.2.0) | m. | .65 | (12.3.0) | a. | .07 |
| (14.0.0) | m.w. | .69 | (14.1.0) | a. | .06 | (14.2.0) | w. | .52 | | | |
| (16.0.0) | a. | .00 | (16.1.0) | a. | .06 | (16.2.0) | a. | .00 | | | |
| (18.0.0) | m.w.-w. | .69 | (18.1.0) | a. | .06 | (18.2.0) | w. | .52 | | | |
| (20.0.0) | m. | .85 | (20.1.0) | a. | .01 | (20.2.0) | m.w. | | | | |
| (22.0.0) | a. | .04 | | | | | | | | | |

(1) Also from Weissenberg photographs, Cu $K$ radiation.

(2) ($0kl$) with $k$ odd } required to be absent
($h0l$) with $l$ odd }

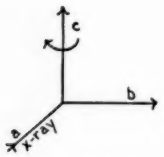



| Equatorial zone | | | | 2nd layer line | | | | 4th layer line | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $S/64F^2_I$ | | | | $S/64F^2_I$ | | | | $S/64F^2_I$ |
| Plane | Int. | $Z=0.20$ | $Z=0.22$ | Plane | Int. | $Z=0.20$ | $Z=0.22$ | Plane | Int. | $Z=0.22$ |
| | | | | (021) | S. | 0.23 | 0.25 | (041) | m.s. | 0.70 |
| (002) | v.s. | 0.65 | 0.87 | (022) | v.s. | .50 | .67 | (042) | m.w. | .25 |
| (202) | m.w. | .19 | .25 | | | | | | | |
| | | | | (023) | m.w. | .09 | .17 | (043) | m. | .50 |
| (004) | m.s. | .10 | .54 | (024) | m-m.s. | .08 | .41 | (044) | w. | .16 |
| | | | | (025) | v.w. | .00 | .09 | (045) | w. | .25 |
| (006) | m. | .10 | .17 | (026) | m.w. | .08 | .15 | (046) | a. | .05 |

Reflections were present from a number of planes in the 1, 3, and 5 layer lines ((212), (232), (113) etc.), they are not included since trustworthy intensity observations could not be made for them.

TABLE VII.—(*Continued.*)

(3) $(hk0)$ with $h$ odd, $(0kl)$ with $k$ odd } required to be absent




| Equatorial zone | | | 1st layer line | | | 2nd layer line | | | 3rd layer line | | | 4th layer line | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plane | Int. | $S/16F^2_I$ | Plane | Int. | $S/16F^2_I$ | Plane | Int. | $S/16F^2_I$ | Plane | Int. | $S/16F^2_I$ | Plane | Int. | $S/16F^2_I$ |
| (020) | v.s. | 0.79 | (021) | v.s. | 0.25 | (022) | v.s. | 0.67 | (023) | m. | 0.17 | (024) | m.s. | 0.41 |
| (220) | w. | .16 | | | | (222) | v.w. | .13 | | | | | | |
| (230) | m.s. | .32 | (231) | m.s. | .37 | (232) | w. | .30 | (233) | w. | .43 | (234) | v.w. | .18 |
| (430) | m.s. | .45 | (431) | m.s. | .52 | (432) | w. | .36 | | | | | | |
| (040) | m.w. | .29 | (041) | m.s. | .70 | (042) | w. | .25 | (043) | m. | .50 | (044) | a. | .16 |
| (240) | v.w. | .07 | (241) | w. | .18 | (242) | v.w. | .06 | | | | | | |
| (250) | m.s. | .62 | (251) | v.w. | .06 | | | | | | | | | |
| (450) | m. | .87 | (451) | v.w. | .10 | | | | | | | | | |
| (060) | a. | .00 | (061) | m.w. | .95 | | | | | | | | | |

### *1,3 diiodobenzene*

Rhombic pyramidal lattice dimensions

$a = 17.20$A (measured)
$b = 7.08$
$c = 6.21$

$4C_6H_4I_2$ in the unit of structure

Types of absences
$(hkl)$ with $(h+k)$ odd
$(h0l)$ in odd orders.

*Crystal symmetry.* 1,3 diiodobenzene is listed by Groth as crystallizing in the bipyramidal division of the rhombic system. The x-ray results, however, require the crystals to be pyramidal. Dr. A. Hettich of the *Mineralögische-Geológisches Institut der Technischen Hochschule*, München, kindly tested the piezoelectric properties of a sublimed sample of the substance, using the method of Giebe and Scheibe.[20] A positive effect was found somewhat less in intensity than that given by sucrose.

*Space group and atomic arrangement.* Possible space groups are:

| | | | |
|---|---|---|---|
| Orthorhombic | holohedral | C $m\,m\,m$ and | C $m\,c\,m$ |
| | hemihedral | C $m\,m$ , | C $m\,c$ |
| | | A $m\,m$ , | A $m\,a$ |
| Monoclinic | holohedral | C $2/c$ , | C $2/m$ |

The absence of odd order reflections from $(00l)$ requires the iodine atoms to have a translation of $\tau c/2$ and the intensities of the various reflections require their positions to be fixed by parameters in both the $a$ and $b$ directions. For these reasons the iodine atoms cannot be in the 8 equivalent positions of C $m\,m\,m$, the general positions of C $m\,m$, A $m\,m$ or A $m\,a$ or in 8 equivalent positions other than

$$uv\tfrac{1}{4};\ \bar{u}\bar{v}\tfrac{1}{4};\ u+\tfrac{1}{2}, v+\tfrac{1}{2}, \tfrac{1}{4};\ \tfrac{1}{2}-u, v+\tfrac{1}{2}, \tfrac{1}{4}\ \bar{u}\bar{v}\tfrac{3}{4};$$
$$u\bar{v}\tfrac{3}{4};\ \tfrac{1}{2}-u, \tfrac{1}{2}-v, \tfrac{3}{4};\ u+\tfrac{1}{2}, \tfrac{1}{2}-v, \tfrac{3}{4} \quad \text{(a)}$$

of C $m\,c\,m$. The general positions of C $m\,c$ contain (a) above as a special and only case if one type of atom alone is considered in the lattice. Arrangement (a) also results from the general positions of C $2/c$, and C $2/m$ for special parameter values. The intensities of the various reflections do not permit of combinations of iodine atoms in four equivalent positions.

If the compound is truly orthorhombic the minimum molecular symmetry is that of the point group $C_s - m$ (space group C $m\,c$), a plane of symmetry. It seems improbable, since logical positions are not afforded for the carbon atoms, that the structure could be derived from space group C $m\,c\,m$. Possible positions for the carbon atoms in C $m\,c$ are

$$4(a)\ ouv;\ o, \bar{u}, v+\tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}+u, v;\ \tfrac{1}{2}, \tfrac{1}{2}, -u, v+\tfrac{1}{2}$$

and the general positions.

*Parameter determinations.* There are two parameters for the iodine atoms to be determined. The intensities of $(h00)$ in various orders,

[20] E. Giebe and A. Scheibe, Zeits. f. Physik **33**, 760 (1925).

| Some Interatomic Distances | | | |
|---|---|---|---|
| C-C | | I-I | |
| Figure | Distance | Figure | Distance |
| 1-2* | 3.71 | A-E | 4.15 |
| 1-2' | 3.71 | | 4.15 |
| 1-3 | 3.60 | A-C | 4.38 |
| 1-4 | 4.20 | | 4.38 |
| 1-5 | 4.01 | A-F | 4.58 |
| 1-6 | 3.74 | A-B' | 5.30 |
| | | A-I' | 6.50 |

*Assumed

| Parameter Values | | | |
|---|---|---|---|
| Atom | x | y | z |
| I | .172 | .04 | .22 |
| $C_a$ | .009 | .11 | .37 |
| $C_b$ | -.059 | .09 | .47 |
| $C_c$ | -.074 | -.02 | .62 |
| $C_d$ | -.009 | -.11 | .64 |
| $C_e$ | .059 | -.09 | .53 |
| $C_f$ | .074 | .02 | .38 |

Assumed

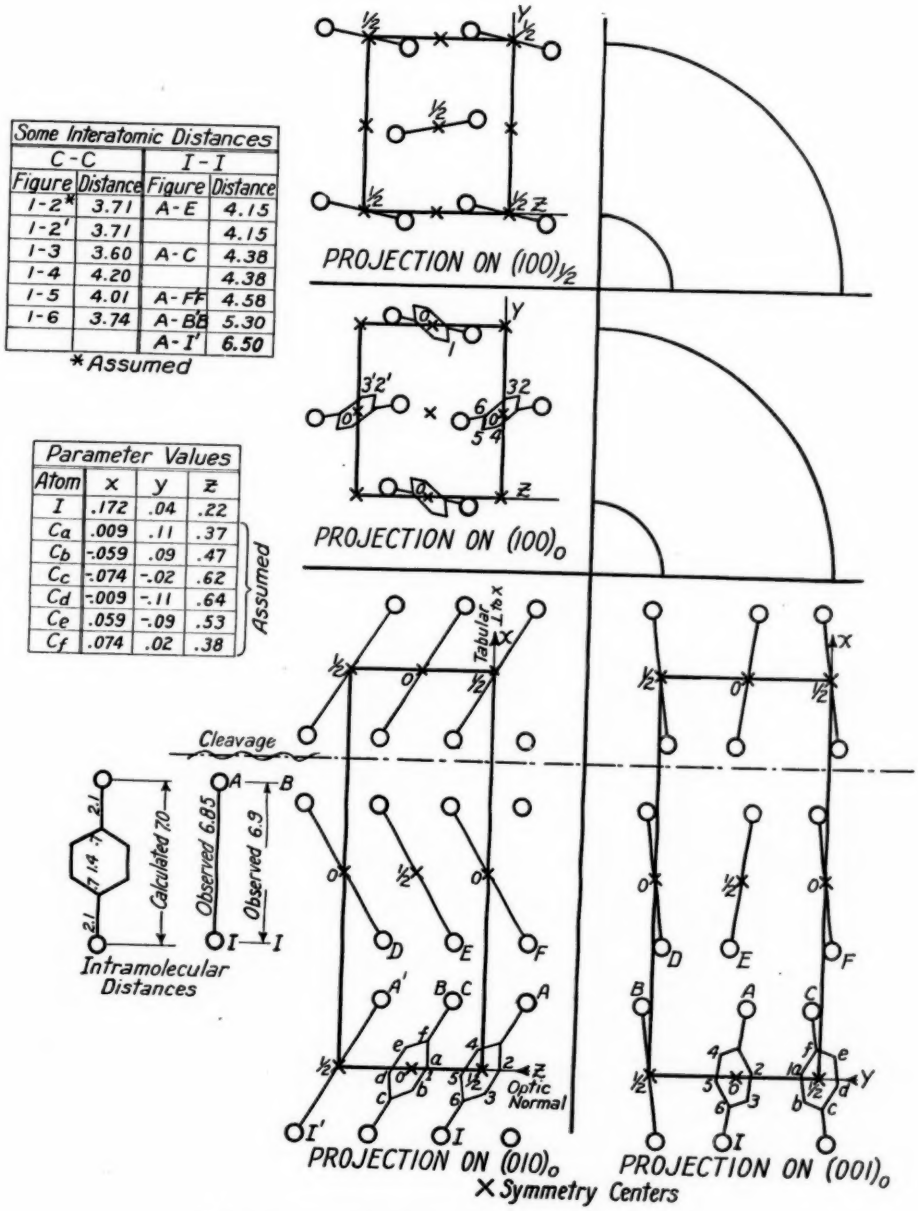
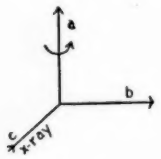



FIG. 12. The crystal structure of 1,4 diiodobenzene.

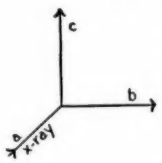
TABLE VIII. *Oscillating crystal photographic data from 1,3 diiodobenzene.*
Mo $K$ radiation, 45° oscillation.

(1)




($hk0$) with $(h+k)$ odd absent

(2)




($0kl$) with $k$ odd required to be absent. (Note below)

| Equatorial zone | | | 1st layer line | | | 2nd layer line | | | 3rd layer line | | | 2nd layer line | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ | Plane | Int. | $S/64F^2_I$ |
| (200) | m.w. | 0.31 | | | | | | | | | | | | |
| (400) | w. | .14 | (310) | w. | 0.10 | (420) | v.w. | 0.09 | | | | | | |
| (600) | v.s. | .96 | (510) | v.w. | .04 | (620) | s. | .61 | | | | (602) | v.s. | 0.96 |
| (800) | s. | .50 | (710) | a. | .01 | (820) | m. | .32 | (730) | a. | 0.06 | (802) | m.s. | .50 |
| (10.0.0) | a. | .04 | (910) | w. | .09 | (10.2.0) | a. | .03 | (930) | m. | .58 | (10.0.2) | a. | .04 |
| (12.0.0) | s. | .85 | (11.1.0) | v.w. | .07 | (12.2.0) | m. | .55 | (11.3.0) | m.w. | .40 | (12.0.2) | m.s. | .85 |
| (14.0.0) | m.s. | .72 | (13.1.0) | a. | .00 | (14.2.0) | m.w. | .46 | (13.3.0) | a. | .01 | (14.0.2) | m. | .72 |
| (16.0.0) | a. | .00 | (15.1.0) | v.w. | .08 | (16.2.0) | a. | .00 | (15.3.0) | m.w. | .49 | (16.0.2) | a. | .00 |
| (18.0.0) | m. | .69 | (17.1.0) | v.w. | .08 | (18.2.0) | w. | .44 | (17.3.0) | m.w. | .51 | (18.0.2) | m.w. | .69 |
| (20.0.0) | m. | .87 | (19.1.0) | a. | .00 | (20.2.0) | w. | .56 | (19.3.0) | a. | .00 | (20.0.2) | m.w. | .87 |
| (22.0.0) | a. | .04 | (21.1.0) | a. | .05 | (22.2.0) | a. | .03 | | | | | | |
| (24.0.0) | a. | .50 | | | | | | | | | | | | |
| (26.0.0) | w. | 1.00 | | | | | | | | | | | | |

The intensities in the equatorial zone are given under (1). Some reflections other than ($0kl$) Int. $a$ were present in the 1st and 3rd layer lines. These are not listed since they could not be identified with certainty.

particularly the absence of the 10th, 16th, and 22nd orders requires $u=0.172\pm0.002$ or $0.078\pm0.002$. The absence of (13.1.0) with the presence of (9.1.0), (11.1.0), (15.1.0) etc. requires,

$$u=0.172\pm0.002.$$

The observed low intensities of ($hk0$) with $k=1$, the approximate equality in the intensities of (11.3.0) and (14.2.0), the very high intensity of (350) and low intensity of (351) require,

$$v=0.20\pm0.01.$$

The value cannot be exactly 0.20 since (351) is present.

Structure factors are of the type—

$l$ even $A/8F_I=\cos 2\pi n(hu)\cos 2\pi n(kv)$

$l$ odd $B/8F_I=\cos 2\pi n(hu)\sin 2\pi n(kv)$.

The concordance between observed intensities of reflection and calculated structure factors is shown in Tables VIII and IX.

*Optical properties.* 1,3 diiodobenzene has been described as optically negative with the interference figure of the obtuse bisectrix visible through $(100)_{sp.G.}$, the plane of the optic axis being $(001)_{sp.G.}$. The indices of refraction determined by the immersion method under the microscope are $\alpha=1.611$ $(n_D)$, $\beta>1.78$, $\gamma>1.80$. The high birefringence is determined by the orientation of the benzene rings, which thus

TABLE IX. *Laue photographic data from 1,2 diiodobenzene.*
W. anticathode 26,000 v. peak. X-ray beam at about 7° to normal to (100).

| Plane | $d_{hkl}$ | $n$ | Est. Int. | $S/64F^2_I$ |
|---|---|---|---|---|
| (223) | 1.75 | 0.52 | 3 | 0.11 |
| | | .66 | 6 | |
| | | .72 | 6 | |
| | | .90 | 8 | |
| ($2\bar{4}\bar{1}$) | 1.67 | .76 | 7 | 0.28 |
| ($3\bar{1}\bar{4}$) | 1.47 | .67 | 5 | 0.10 |
| ($3\bar{5}0$) | 1.37 | .68 | >10 | 1.00 |
| ($3\bar{5}1$) | 1.34 | .78 | 0.5 | 0.00 |
| ($3\bar{3}\bar{4}$) | 1.27 | .74 | 7 | 0.65 |
| ($3\bar{5}2$) | 1.25 | .69 | 9 | 1.00 |
| ($4\bar{4}3$) | 1.28 | .62 | 1 | 0.12 |
| ($5\bar{3}\bar{4}$) | 1.22 | .74 | 3 | 0.27 |
| ($3\bar{1}\bar{5}$) | 1.20 | .62 | 5 | 0.91 |
| ($5\bar{1}\bar{5}$) | 1.15 | .68 | 3 | 0.37 |
| ($4\bar{6}1$) | 1.12 | .70 | 1 | 0.12 |
| ($6\bar{2}\bar{5}$) | 1.08 | .73 | 3 | 0.35 |
| ($8\bar{6}3$) | 0.92 | .72 | 0.5 | 0.48 |
| (023)* | 3.57 | .54 | 5 | 0.35 |
| (041) | 3.40 | .52 | 6 | 0.90 |

* A second photograph at a greater angle to the normal to (100).

| Some Interatomic Distances | | | |
|---|---|---|---|
| C-C | | I-I | |
| Figure | Distance | Figure | Distance |
| a-d' | 3.70 | A-B | 4.11 |
| | 3.70 | | 4.11 |
| d-a' | 3.70 | A-C | 4.25 |
| | 3.70 | | 4.25 |
| c-b' | 4.05 | A-D | 4.40 |
| b-c' | 4.05 | | 4.40 |

| Parameter Values | | | | |
|---|---|---|---|---|
| Atom | X | Y | Z | |
| I | .172 | .200 | .00 | |
| $C_a$ | .000 | .220 | .07 | Assumed |
| $C_b$ | .071 | .239 | .17 | |
| $C_c$ | .071 | .276 | .39 | |
| $C_d$ | .000 | .295 | .49 | |

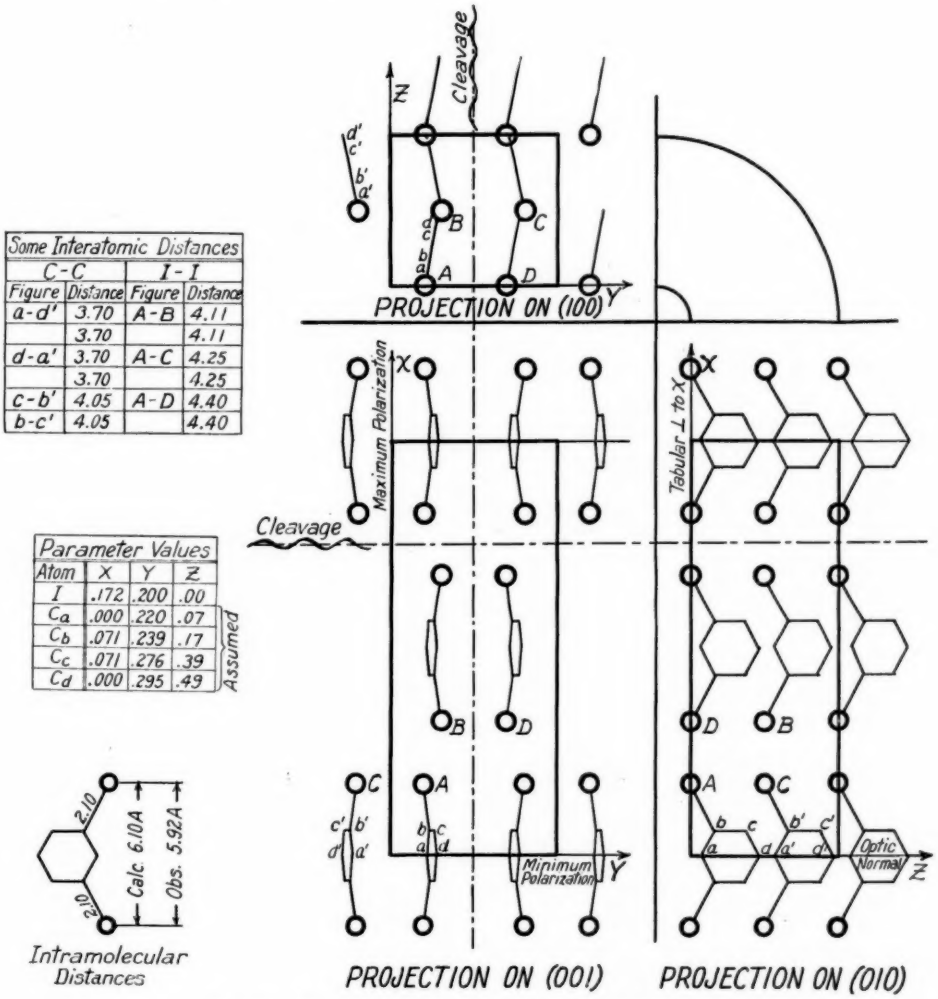



FIG. 13. The crystal structure of 1,3 diiodobenzene.

must be approximately but not exactly parallel to $(010)_{sp.G.}$.

The structure as determined is shown in Fig. 13. The perfect cleavages parallel to (010) and (100) are readily explained. The indicated positions of the carbon atoms are ones giving an intermolecular distance of about 3.70A.

*1,2 diiodobenzene*

Monoclinic prismatic
Lattice dimensions
$a = 8.29$A
$b = 12.23$ ($d_{(010)} = 12.20$A)
$c = 7.91$
$\gamma = 93° 56'$ (Goldschmidt) $\gamma = 93.8°$ (Weissenberg photographs).

$4C_6H_4I_2$ in unit of structure

A satisfactory structure determination was not made for 1,2 diiodobenzene. The lattice is apparently the simple monoclinic one, the space group probably $P2_1/m$ or $P2/m$. In any case the positions of the iodine atoms are determined by six parameters. The intensities of the first ten orders of interference from (010) apparently are: 1, a.; 2, a.; 3, a.; 4, v.s.; 5, w.; 6, m.; 7, a.; 8, m.s.; 9, a.; 10, m. If iodine atoms are at $y_1$, $-y_1$, $y_2$, and $-y_2$ the values of $y$ must be about

$$y_1 = 0.13, \quad y_2 = 0.37 \text{ or } -0.37,$$

$$y_1 = 0.37, \quad y_2 = 0.13 \text{ or } -0.13.$$

The crystals are optically positive which indicates that the planes of the benzene rings are not approximately parallel.

## Discussion

The separation of the iodine atoms in the various compounds studied are listed in Table X. Molecular iodine affords the most extensive test of the methods used in the analysis of electron diffraction data. The I−I distance determined by us is in good agreement with both the band spectra and x-ray diffraction results.

Table X. *Summary of iodine to iodine distances (A).*

| Molecule | Electron diffraction | X-ray crystal structure | Band spectra |
|---|---|---|---|
| Iodine | 2.64A | 2.70A* | 2.66A |
| 1,4 Diiodobenzene | 6.85 | 6.85 | |
| 1,3 Diiodobenzene | 5.97 | 5.92 | |
| 1,2 Diiodobenzene | 4.00 | | |

* P. M. Harris, E. Mack, Jr., and F. C. Blake, J. A. C. S. **50**, 1583 (1928).

Electron and x-ray diffraction data obtained from 1,3 and 1,4 diiodobenzenes indicate that the atomic arrangements within these molecules are invariant with vaporization of the solid. The I−C distances for the diiodobenzenes are 2.00A in all cases and the assumed C−H, and C−C distances are verified since they are consistent with the results obtained. These results are in harmony with the concept of approximately constant homopolar distances of particular types in such compounds.

In 1,4 and 1,3 diiodobenzene the line joining the center of an iodine atom to the adjacent carbon atom, which might be referred to as the valence direction, is symmetrically disposed in the plane of the benzene ring. In 1,2 diiodobenzene, however, this direction is distorted by about 10° from the symmetrical position. The I−I distance in this molecule is 4.00A, which is far greater than the value 3.52A required by the symmetrical arrangement and slightly less than 4.10A, the minimum intermolecular separation of the iodine atoms in the other crystalline diiodobenzenes.

It was not possible to determine whether the deformations of the valence directions in 1,2 diiodobenzene are in or out of the plane of the benzene ring. The absence of optical and of geometrical isomerism in simple derivatives of such a compound, however, have usually been taken as evidence for a coplanar atomic arrangement. Some support is also given to this point of view by the structure of hexamethylbenzene.[15]

*This irregularity in ortho substitution is perhaps the first clear physical evidence for the phenomenon of "steric hindrance."* In general the reactivity of a group on a benzene ring is markedly affected by the presence of groups ortho to it. This has perhaps been most clearly shown by the work of V. Meyer[21] and his students on the esterification of carboxylic acids. In 1,2 diiodobenzene it is impossible to meet the requirements imposed by the I−I separation, that is the steric effect, without modification of the molecule in a manner that would probably affect its reactivity.

From consideration of heats of combustion for a number of benzene derivatives Stuart[22] concluded that the C−$CH_3$ valence directions are not distorted in 1,2 xylene. He calculated that an energy greater than 2000 cal./mole would be required for a 10° distortion of that direction. This value probably will serve to indicate there is a considerable increase in the potential energy of 1,2 diiodobenzene as compared with the 1,3 and 1,4 derivatives.

In principle, crystal structure analysis offers an almost unique method for determining the atomic arrangement within complex molecules. Unfortunately, it is limited in application by the necessary simultaneous determination of the molecular orientations. There is considerable hope that regularities will be found in the intermolecular distances of approach in solids of a particular type. Careful study of Figs. 12 and 13 will perhaps make apparent the regularities in the packing of iodine atoms of separate molecules. Six iodine atoms are so arranged that their separations are between 4.11 and 4.6A. This minimum distance of approach is approximately the same as that found in other iodine substituted compounds.[17,23,24] Although the assumption of a minimum intermolecular C−C distance was

[21] V. Meyer, Berichte **27**, 510, 1580 (1894); **28**, 1255, 2774, 3197 (1895).

[22] H. A. Stuart, Phys. Rev. **38**, 1372 (1931).

[23] H. P. Klug, J. Am. Chem. Soc. **55**, 1430 (1933).

[24] E. Halmöy and O. Hassel, Zeits. f. physik. Chemie **B16**, 234 (1932).

used in the analysis of the crystal structures, the structure of 1,3 diiodobenzene really serves independently to verify it.

The methods that we have used are perhaps capable of extension to the study of a larger number of compounds containing two or more heavy atoms. In particular, observations on substances such as 2,6 diiodobenzoic acid would probably lead to important information bearing on steric hindrance.

# Electron Diffraction and Molecular Structure

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The molecular structures of cis- and trans- dibromoethylene, tribromoethylene, vinyl bromide, tetrachloroethylene and trichloroethylene have been determined by the method of electron diffraction in gases. It has been found that the diffraction pictures of these substances can be satisfactorily represented by plane structures having the following interatomic distances: C=C 1.3, C−Br 2.0 and C−Cl 1.8A. The diffraction in carbon tetrachloride has been investigated with several widely differing electron velocities.

## INTRODUCTION

INVESTIGATIONS of electron diffraction in gases have led to the solution of many problems in the realm of molecular structure as the work of Wierl[2] has shown. The present investigation was undertaken to determine the structures of several chlorine and bromine derivatives of ethylene and particularly to study the variation of certain interatomic distances in closely related compounds.

Structure determinations by the method of electron diffraction in gases depend upon a comparison of the relative intensity distribution curve, calculated for a definite molecular model, with the observed angular intensity curve. The relative intensity $I$[3] as a function of the scattering angle $\theta$, of electrons diffracted by a gas molecule is given by

$$I=k\sum_i\sum_j\psi_i\psi_j(\sin x_{ij}/x_{ij}), \qquad (1)$$

where $k$ is a constant under experimental conditions, the $\psi$'s are the electron scattering coefficients of the atoms and

$$x_{ij}=(4\pi l_{ij}\sin\theta/2)/\lambda. \qquad (1a)$$

Mott[4] has derived the relation

$$\psi_i=(Z_i-f_i)/((\sin\theta/2)/\lambda)^2, \qquad (1b)$$

in which $Z_i$ is the atomic number and $f_i$ is the x-ray scattering factor or the atomic form factor. In Eq. (1a) $l_{ij}$ is the distance from the $i$th atom to the $j$th atom and $\lambda$ is the de Broglie wave-length of the incident electron beam.

## EXPERIMENTAL PROCEDURE

The method of studying electron diffraction in gases consists essentially in allowing a fine beam of electrons of uniform velocity to intersect the gas stream and recording the diffracted electrons on a photographic plate which is perpendicular to the incident electron path. The apparatus used follows in essentials the design of Wierl.[2] A hydrogen discharge served as a source of electrons which were accelerated by the high potential from a source of constant potential d.c.[5] The primary of a Snook 10 kw 140 kv transformer was supplied with 500 cycle a.c. from Crocker-Wheeler motor-generator Type CB 23. Two kenotrons, General Electric Company Type KC-1, were connected to the secondary of the transformer to give full-wave rectification. Specially insulated transformers supplied the kenotron filaments. The ripplance in the kenotron output was smoothed out by five 0.05 $\mu f$ glass condensers. An electrostatic voltmeter, consisting of two fixed 5 inch copper spheres and two 2.5 inch spheres on a bifilar suspension indicated the voltage across the hydrogen discharge tube. The voltmeter was calibrated by reference to a Taylor High Voltage Resistor of 50 megohms

[1] National Research Fellow in Chemistry.

[2] R. Wierl, Ann. d. Physik [5] **8**, 521 (1931); ibid. [5] **13**, 453 (1932).

[3] H. Mark and R. Wierl, Fortschr. Chem. Physik physik. Chemie **B21**, 4 (1931).

[4] N. F. Mott, Proc. Roy. Soc. (London) **A127**, 658 (1930).

[5] A. W. Hull, Gen. Elec. Rev. **19**, 193 (1916).

connected in series with a sensitive milliammeter.

The electrons entered the diffraction chamber through two holes 0.2 mm and 0.1 mm in diameter. The gas at a pressure of about 150 mm of mercury entered the diffraction chamber through a fine nozzle placed at right angles to the electron nozzle. Immediately above the gas nozzle (0.1 mm aperture) was a liquid air trap which condensed most of the gas. The electrons were recorded on an Eastman 33 plate which was 25.7 cm from the gas nozzle. The diffraction chamber was evacuated by a high speed diffusion pump[6] which was backed by an oil pump. The hydrogen discharge tube was evacuated independently of the diffraction chamber.

The diffraction pictures were taken at a pressure of $10^{-5}$ mm of mercury and the length of exposure varied from a fraction of a second to two seconds. A mechanical shutter which interrupted the electron beam controlled the time of exposure. The diffraction pictures were photometered on a Zeiss recording microphotometer and the photometer curves analyzed by enlarging. This procedure avoided the physiological error inherent in analyzing the diffraction photograph itself.

TABLE I. *Carbon tetrachloride*, λ, A.

| $x$ | 0.05805 | 0.05991 | 0.06195 | 0.06420 | 0.06670 | 0.06951 | 0.07632 | 0.08055 | Calc. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $(\sin\theta/2)/\lambda$ | | | | |
| 7.4 | 0.197 | 0.198 | 0.198 | 0.198 | 0.198 | 0.198 | 0.198 | 0.197 | 0.1975 |
| 13.6 | .363 | .364 | .363 | .363 | .362 | .363 | .364 | .362 | .3630 |
| 20.3 | .540 | .542 | .542 | .541 | .543 | .542 | .542 | | .5415 |
| 26.2 | .698 | .700 | .700 | .700 | .700 | .700 | | | .6993 |
| 32.7 | .874 | .873 | | | | | | | .8720 |

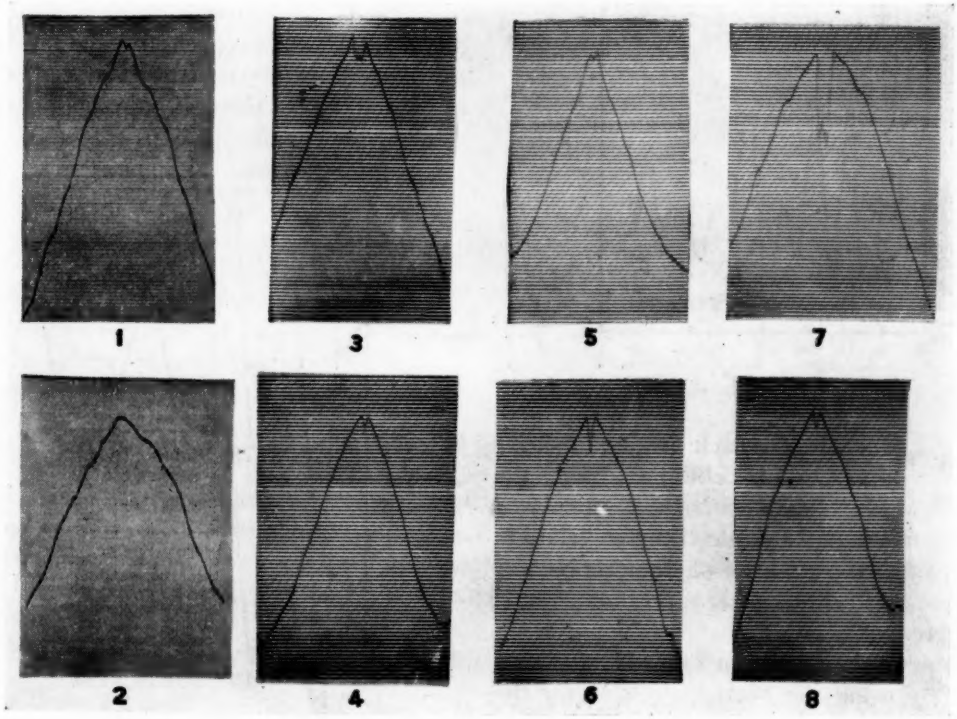


FIG. 1. Photometer curves of electron diffraction photographs. 1 and 2, carbon tetrachloride; 3, cis-dibromoethylene; 4, trans-dibromoethylene; 5, tribromoethylene; 6, vinyl bromide; 7, tetrachloroethylene; 8, trichloroethylene. Electron accelerating potential 45 kilovolts for all pictures except No. 2, 25 kilovolts.

[6] I. Estermann and H. T. Byck, Rev. Sci. Inst. 3, 482 (1932).

## Results and Discussion

The preliminary work was an investigation of the diffraction of carbon tetrachloride and its dependence upon the electron accelerating potential. A series of pictures were taken at intervals of 2.5 kv from 20 to 45 kv. The first column of Table I gives the $x$ values for the maxima calculated for a regular tetrahedron; the last column gives the $(\sin \theta/2)/\lambda$ values calculated for a carbon chlorine distance of 1.82A. The other columns record the average values of $(\sin \theta/2)/\lambda$ obtained from several pictures at each wave-length. The agreement of

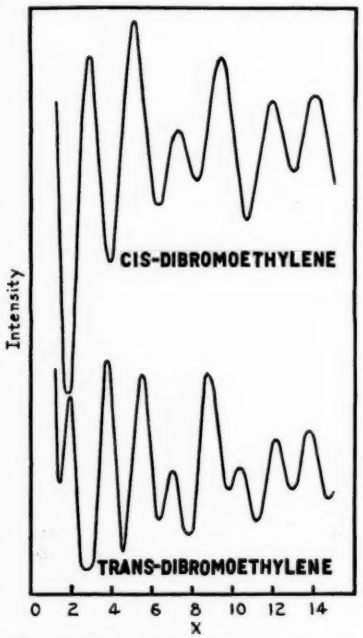


Fig. 2. Theoretical intensity curves.

the $(\sin \theta/2)/\lambda$ values for each maximum shows that true diffraction is obtained, and the agreement of the values with those calculated affords a check on the de Broglie relation. Curves 1 and 2 of Fig. 1 are photometer records for carbon tetrachloride at 45 and 25 kv, respectively.

The values of $x$ recorded in Table II have been obtained by using the Mott expression for the electron scattering coefficient, $\psi$. The $x$ values obtained by replacing $\psi$ with $Z$ are only slightly different for the first few maxima. The intensity curves shown in Figs. 2, 3 and 4 are calculated by the latter simpler method. The $(\sin \theta/2)/\lambda$ values

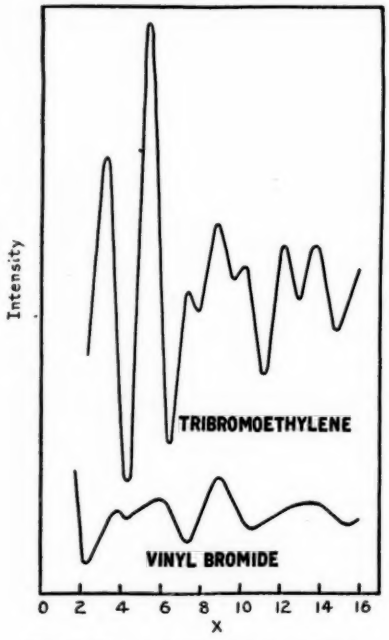


Fig. 3. Theoretical intensity curves.

of Table II are averages obtained from several pictures at each wave-length. The $l$ values give the value of the C=C distance in A. The error is estimated from the deviations of individual results from the mean.

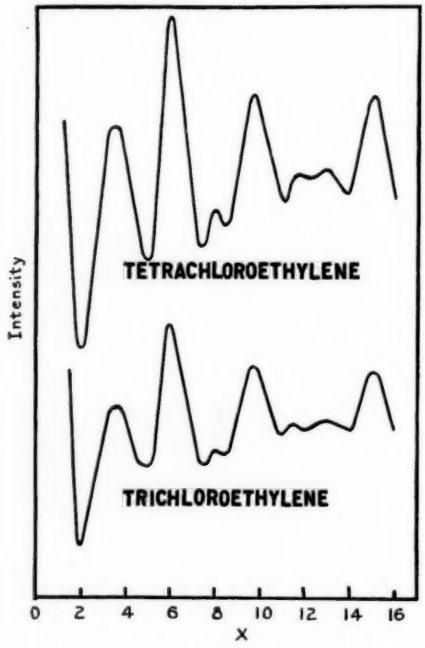


Fig. 4. Theoretical intensity curves.

TABLE II. λ, A.

| | 0.05991 sin θ/2 | | 0.05805 sin θ/2 | | 0.05635 sin θ/2 | |
|---|---|---|---|---|---|---|
| $x$ | λ | $lA$ | λ | $lA$ | λ | $lA$ |
| | | | *Cis-Dibromoethylene* | | | |
| 2.90 | 0.174 | 1.33 | 0.174 | 1.33 | 0.174 | 1.33 |
| 4.90 | .296 | 1.32 | .297 | 1.31 | .298 | 1.31 |
| 7.30 | .442 | 1.31 | .439 | 1.32 | .440 | 1.32 |
| 9.35 | .569 | 1.30 | .563 | 1.32 | .564 | 1.31 |
| 12.10 | .782 | 1.23 | .729 | 1.32 | .731 | 1.32 |
| 14.10 | | | | | .847 | 1.32 |
| | | | C=C=1.32±0.08A | | | |
| | | | C−Br=2.05±0.08A | | | |
| | | | Br−Br=3.67±0.08A | | | |
| | | | *Trans-Dibromoethylene* | | | |
| 1.85 | 0.112 | 1.31 | 0.109 | 1.35 | 0.114 | 1.29 |
| 3.75 | .229 | 1.30 | .226 | 1.32 | .224 | 1.33 |
| 5.50 | .330 | 1.33 | .339 | 1.29 | .336 | 1.30 |
| 6.95 | .413 | 1.34 | .417 | 1.33 | .419 | 1.32 |
| 8.75 | .529 | 1.32 | .528 | 1.32 | .529 | 1.32 |
| 10.40 | .625 | 1.32 | .627 | 1.32 | .630 | 1.31 |
| 12.10 | | | | | .733 | 1.31 |
| | | | C=C=1.32±0.08A | | | |
| | | | C−Br=2.05±0.08A | | | |
| | | | Br−Br=4.97±0.08A | | | |
| | | | *Tribromoethylene* | | | |
| 3.25 | 0.201 | 1.28 | 0.201 | 1.28 | 0.196 | 1.31 |
| 5.40 | .325 | 1.34 | .332 | 1.28 | .329 | 1.30 |
| 7.65 | .458 | 1.32 | .454 | 1.33 | .461 | 1.31 |
| 8.85 | .534 | 1.28 | .533 | 1.29 | .542 | 1.26 |
| 10.00 | .604 | 1.31 | .597 | 1.32 | .606 | 1.30 |
| 12.15 | | | .736 | 1.30 | .736 | 1.30 |
| | | | C=C=1.32±0.08A | | | |
| | | | C−Br=2.05±0.08A | | | |
| | | | Br−Br=3.67±0.08A | | | |
| | | | Br−Br=4.97±0.08A | | | |

| | 0.05991 sin θ/2 | | 0.05805 sin θ/2 | | 0.05635 sin θ/2 | |
|---|---|---|---|---|---|---|
| $x$ | λ | $lA$ | λ | $lA$ | λ | $lA$ |
| | | | *Vinyl Bromide* | | | |
| 3.90 | 0.235 | 1.32 | 0.230 | 1.35 | 0.226 | 1.37 |
| 5.75 | .349 | 1.31 | .345 | 1.32 | .349 | 1.31 |
| 8.90 | .534 | 1.32 | .526 | 1.34 | .537 | 1.32 |
| 13.75 | .820 | 1.33 | | | .812 | 1.35 |
| | | | C=C=1.32±0.08A | | | |
| | | | C−Br=2.05±0.08A | | | |
| | | | *Tetrachloroethylene* | | | |
| 3.35 | 0.204 | 1.31 | 0.203 | 1.31 | 0.202 | 1.32 |
| 6.00 | .364 | 1.31 | .363 | 1.32 | .363 | 1.32 |
| 9.75 | .590 | 1.31 | .588 | 1.32 | .586 | 1.32 |
| 13.00 | .783 | 1.32 | .783 | 1.32 | .783 | 1.32 |
| 15.10 | | | .905 | 1.33 | .907 | 1.32 |
| | | | C=C=1.32±0.08A | | | |
| | | | C−Cl=1.82±0.08A | | | |
| | | | Cl−Cl=3.41±0.08A | | | |
| | | | Cl−Cl=4.52±0.08A | | | |
| | | | *Trichloroethylene* | | | |
| 3.40 | 0.202 | 1.34 | 0.203 | 1.33 | 0.199 | 1.36 |
| 6.10 | .364 | 1.33 | .373 | 1.30 | .366 | 1.33 |
| 9.75 | .588 | 1.32 | .609 | 1.27 | .587 | 1.32 |
| 13.05 | .781 | 1.33 | .806 | 1.29 | .780 | 1.33 |
| | | | C=C=1.32±0.08A | | | |
| | | | C−Cl=1.82±0.08A | | | |
| | | | Cl−Cl=3.41±0.08A | | | |
| | | | Cl−Cl=4.52±0.08A | | | |

Eq. (1) for cis-dibromoethylene gives

$$\frac{I}{k}=2\psi^2_{C}\left(1+\frac{\sin x}{x}\right)+2\psi^2_{Br}\left(1+\frac{\sin 2.78x}{2.78x}\right)+4\psi_C\psi_{Br}\left(\frac{\sin 1.55x}{1.55x}+\frac{\sin 2.28x}{2.28x}\right)+4\psi_{Br}\psi_H\left(\frac{\sin 1.99x}{1.99x}+\frac{\sin 3.06x}{3.06x}\right) \tag{2}$$

which omits the scattering due to the C−H and H−H periods. The coefficients of $x$ in the sin $x/x$ terms were found to give satisfactory concordance with the measured maxima and corresponds to a plane model with a 110° angle between the single bonds of each carbon atom and the following interatomic distances: C=C 1.3, C−Br 2.0 and Br−Br 3.7A. The C−H distance was taken as 1.1A.

The intensity distribution for trans-dibromoethylene is:

$$\frac{I}{k}=2\psi^2_{C}\left(1+\frac{\sin x}{x}\right)+2\psi^2_{Br}\left(1+\frac{\sin 3.76x}{3.76x}\right)+4\psi_C\psi_{Br}\left(\frac{\sin 1.55x}{1.55x}+\frac{\sin 2.28x}{2.28x}\right)+4\psi_{Br}\psi_H\left(\frac{\sin 1.99x}{1.99x}+\frac{\sin 2.44x}{2.44x}\right) \tag{3}$$

when the same periods are neglected as in the cis compound. The structure of the trans compound differs from the cis only in the Br−Br distance 5.0A. The marked differences in the calculated intensity curves for these stereoisomers (Fig. 2) is readily seen in the diffraction pictures.

For tribromoethylene Eq. (1) becomes

$$\frac{I}{k}=2\psi^2_{C}\left(1+\frac{\sin x}{x}\right)+2\psi^2_{Br}\left(\frac{\sin 2.54x}{2.54x}+\frac{\sin 2.78x}{2.78x}+\frac{\sin 3.76x}{3.76x}\right)+6\psi_C\psi_{Br}\left(\frac{\sin 1.55x}{1.55x}+\frac{\sin 2.28x}{2.28x}\right)+3\psi^2_{Br}, \tag{4}$$

which neglects the hydrogen. Eq. (4) gives good representation of the observed maxima and is based on a plane model with the following distances: C=C 1.3, C−Br 2.0, Br−Br (attached to same carbon atom) 3.4, Br−Br (attached to different carbon atoms) 3.7 and 5.0A. Wierl[2] has found that the distance between the bromine atoms in carbon tetrabromide was 3.35A in good agreement with the value found in tribromoethylene. An appreciably larger distance might be expected for the latter compound because of the distortion of the tetrahedral angle. This effect could not be established in tribromoethylene as an increase in the distance between the bromine atoms attached to the same carbon is compensated by the decrease in the distance between bromine atoms on the adjacent carbon atoms.

For vinyl bromide Eq. (1) becomes

$$\frac{I}{k}=2\psi^2_{C}\left(1+\frac{\sin x}{x}\right)+6\psi_C\psi_H\left(\frac{\sin 0.82x}{0.82x}+\frac{\sin 1.61x}{1.61x}\right)+2\psi_{Br}\psi_C\left(\frac{\sin 1.55x}{1.55x}+\frac{\sin 2.88x}{2.88x}\right)+2\psi_{Br}\psi_H\left(\frac{\sin 1.99x}{1.99x}+\frac{\sin 2.44x}{2.44x}+\frac{\sin 3.06x}{3.06x}\right)+\psi^2_{Br}+3\psi^2_{H}, \tag{5}$$

which reproduced the observed maxima satisfactorily and is based on a plane model with 110° angle between atoms attached to the same carbon atom and having the following interatomic distances C=C 1.3, C−Br 2.0, C−H 1.1A.

The intensity distribution for tetrachloroethylene is

$$\frac{I}{k}=2\psi^2_{C}\left(1+\frac{\sin x}{x}\right)+8\psi_C\psi_{Cl}\left(\frac{\sin 1.38x}{1.38x}+\frac{\sin 2.11x}{2.11x}\right)+4\psi^2_{Cl}\left(1+\frac{\sin 2.26x}{2.26x}+\frac{\sin 2.58x}{2.58x}+\frac{\sin 3.42x}{3.42x}\right), \tag{6}$$

which corresponds to a plane structure with 110° angle between the chlorine atoms attached to the same carbon atom and having the following interatomic distances: C=C 1.3, C−Cl 1.8, cis Cl−Cl 3.4, trans Cl−Cl 4.5A. Wierl[2] found 3.3A for the chlorine-chlorine distance in cis-dichloroethylene and 4.3 for the trans isomer. Distortion of the tetrahedral angle in tetrachloroethylene cannot be established due to the compensation by the other periods, although such an increase of the tetrahedral angle has been found in methylene chloride.[7]

The scattering effect of the hydrogen in trichloroethylene is negligible and the intensity distribution is nearly identical with that of the tetrachloroethylene (Fig. 4). The intensity curve is

[7] P. Debye, Zeits. f. Elektrochemie **36**, 614 (1930).

$$\frac{I}{k}=2\psi^2_{\mathrm{C}}\left(1+\frac{\sin x}{x}\right)+6\psi_{\mathrm{C}}\psi_{\mathrm{Cl}}\left(\frac{\sin 1.38x}{1.38x}+\frac{\sin 2.11x}{2.11x}\right)$$
$$+2\psi^2_{\mathrm{Cl}}\left(\frac{\sin 2.26x}{2.26x}+\frac{\sin 2.58x}{2.58x}+\frac{\sin 3.42x}{3.42x}\right)+3\psi^2_{\mathrm{Cl}}. \tag{7}$$

The structure of trichloroethylene is the same as that of the tetrachloroethylene.

The diffraction photographs of the chlorine and bromine derivatives of ethylene led to plane structures with the following constant interatomic distances C=C 1.3, C−Br 2.0 and C−Cl 1.8A. These values are in good agreement with the atomic radii formulated by Pauling[8] which give the following values respectively 1.38, 1.91 and 1.76A.

The writer is indebted to Professor G. N. Lewis for suggesting this field of research.

[8] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

# The Raman Spectrum of Tetramethylmethane

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Raman spectra of tetramethylmethane, the mono chloro derivative of tetramethylmethane and *n*-amyl chloride, have been obtained with a spectrograph which gave a dispersion of 14A/mm at λ4500. Filters were employed which permitted the observation of the weaker lines. The rather simple arrangement of very intense quartz water-cooled vacuum mercury arcs is described. The results for tetramethylmethane confirm the predictions of the theory of the vibration spectrum of the hydrocarbons which was developed by Kohlrausch and Barnes.

## INTRODUCTION

KOHLRAUSCH and Barnes[1] have obtained the Raman spectrum of tetramethylmethane, which compound is extremely interesting because of its highly symmetrical character. The above authors have developed a semi-empirical theory of the vibration spectrum of the hydrocarbons from the analysis of the spectrum of this compound and the spectrum of the other lower members of this series of hydrocarbons. The experimental results of Kohlrausch and Barnes leave several points open to question. The purpose of this investigation was to attempt to remove these discrepancies and to verify the predictions of the theory by the use of more adequate experimental procedure.

## EXPERIMENTAL

The present experimental arrangement was designed to permit the use of a moderately high dispersion spectrograph and at the same time permit the use of adequate filters.

The mercury arcs consist of simple U tubes of quartz about 30 cm in length and operate in the vertical position. Two of these U arcs were used in the present investigation, arranged in such a manner that each leg of the U is at a corner of the square formed by the four legs. This arrangement is effectually equivalent to four mercury arcs about 12 cm in length.

These arcs are mounted in a suitable container to permit water cooling. The legs of the U's pass through the bottom of the container and are attached to a vacuum system by means of heavy rubber pressure tubing. The starting of the arcs is accomplished by means of suitable mercury traps, the mercury levels of which could be raised or lowered as necessary. The electrodes are simply the mercury columns of these traps (line connections being made by means of iron rods immersed in the open arms of the traps).

These arcs were operated at a current density of about 30 amperes per cm² of cross section and under such operating conditions have a useful life of from 300 to 400 hours. The black deposit which forms on the walls of the quartz tube after long usage can be removed by means of concentrated hydrofluoric acid followed by heating with an oxy-hydrogen torch which restores the quartz to its original transparency.

The scattering tube was placed in the center of the square formed by the arcs, and surrounded with a cylindrical filter jacket which was designed to permit the use of two separate filter solutions in layers of one cm thickness. The arcs, filter jacket, and scattering tube were surrounded with a cylindrical reflector of silvered glass which has shown itself to be considerably more efficient than the ordinary polished sheet aluminum reflector.

The inside filter jacket contained a 20 percent solution of praseodymium ammonium nitrate[2] and the outside jacket a saturated solution of sodium nitrite.[3] With this combination of filters the excitation is entirely by means of the λ4358

[1] K. W. F. Kohlrausch and D. Barnes, Anales Fisica Y Quimica **30**, 733 (1932).

[2] R. W. Wood and Geo. Collins, Phys. Rev. **42**, 386 (1932).

[3] A. H. Pfund, Phys. Rev. **42**, 581 (1932).

group of mercury. For shifts greater than 2000 $cm^{-1}$ a strong solution of crystal violet was substituted for the praseodymium filter, but in the case of the compounds investigated thus far no lines were found by this means which could not also be observed by means of the praseodymium filter. Exposures were also taken using carbon tetrachloride+iodine in conjunction with the praseodymium filter. In this case the excitation is by means of λ4047 and λ4358 but the λ4358 group is considerably reduced in intensity. The object of taking these exposures was to throw the C–H vibrations into the higher dispersion region of the spectrograph so that more accurate measurements could be made of these shifts. However, it was noted that the use of these shorter wave-lengths produced a slight fluorescence with the compounds used in the present investigation.

The spectrograph[4] employed was a two prism glass instrument (objective F 18) which gave a dispersion of 14A/mm at λ4500. The slit width used was 0.03 mm.

With the experimental arrangement described above, satisfactory unfiltered photographs could be obtained in from one to three hours exposure. When the praseodymium and sodium nitrite filters were used exposures of from 20 to 60 hours were necessary before the continuous background became troublesome. With these filters it required about an hour of exposure in order to photograph the stronger Raman lines.

Measurements of the wave-lengths of the lines were made by means of a large dispersion curve constructed from measurements of the lines of the iron arc spectrum. The frequency shifts tabulated are believed to be accurate $\pm 2$ $cm^{-1}$ except in the cases marked with an asterisk in which cases the errors might be larger because of the faintness and the broad character of these lines. In the case of the sharper lines of good intensity the shifts are probably accurate to a wave number.

The purity of compounds used in work on the Raman effect has in general been relegated to a position of minor importance. However, when intensity ratios as great as 40 to 1 are possible as is the case when the present filter technique is employed, it is easily seen that even one percent of impurity might cause spurious lines to appear, when one considers the fact that some compounds are considerably better scatterers than others.

The compounds used in the present investigation have been carefully purified chemically as far as possible, and then have been fractionally distilled through very efficient fractionating columns.[5] The samples investigated were taken from middle cuts from rather large batches of the compounds. The tetramethylmethane and the mono chloro derivative of tetramethylmethane were prepared and purified by Mr. G. H. Fleming of the Chemistry Department working under the direction of Dr. F. C. Whitmore.[6]

The *n*-amyl chloride was purified by Messrs. J. M. Herndon and G. H. Fleming in the following manner. Commercial *n*-amyl chloride (Sharpless Solvents Corp.) was fractionated through a $75 \times 2.2$ cm packed column with the use of a high reflux ratio. Material of b. p. 103–104°C (734 mm) and $N_d^{20} = 1.4120$ was then treated with silver nitrate solution to remove any traces of secondary and tertiary chlorides and then refractionated. The material used had a b. p. 104.0–104.5°C (732 mm) and $N_d^{20} = 1.4120$, $d_4^{20}$ 0.8846. The only probable impurity would be one percent or less of isoamyl chloride.

## Results

In Table I, the frequency shifts which were observed for the compounds investigated are tabulated. The results obtained by other authors who have investigated these compounds are also tabulated in this table. Intensities of the lines are indicated by means of the number in parentheses.

### Tetramethylmethane

The theory of the vibration spectrum of the hydrocarbons developed by Kohlrausch and Barnes[1] demands for each substance that

$$\tilde{\omega}^2 = [1/(n-1)]\Sigma\omega_i^2,$$

where $n-1$ gives the number of C–C links in the molecule and $\Sigma\omega_i^2$ the sum of the squares of the

[4] D. H. Rank, J. Opt. Soc. Am. **23**, 84 (1933).

[5] Whitmore and Lux, J. Am. Chem. Soc. **54**, 3451–3 (1932).

[6] The details of the preparation and purification of these compounds to be published shortly in the J. Am. Chem. Soc.

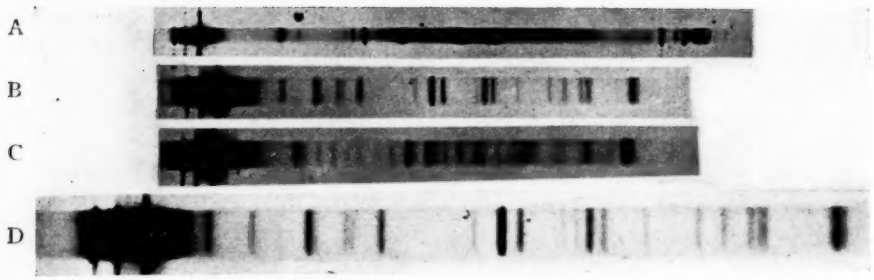


FIG. 1. Raman spectra of (A) tetramethylmethane, (B) tetramethylmethane chloride, (C) *n*-amyl chloride and (D) tetramethylmethane chloride enlarged.

frequencies (vibrations which are doubly or triply degenerate are counted twice or thrice respectively). The above authors have shown $\tilde{\omega}^2$ to be nearly constant for homologous molecules. From the constancy of $\tilde{\omega}^2$ and consideration of the model employed, Kohlrausch and Barnes have predicted the existence of a triply degenerate vibrational frequency $\Delta\tilde{\nu}=400$ cm$^{-1}$ for tetramethylmethane which they were unable to observe in their experimental work. In the present investigation this shift was observed and found to be 415 cm$^{-1}$. (In Fig. 1, A, the spectrum of tetramethylmethane is reproduced and the new frequency shift predicted by the theory is indicated by means of an ink dot above the line.) By taking the present more accurate values for these shifts for tetramethylmethane and calculating $\tilde{\omega}^2$, a value of $96.2\times10^4$ is obtained which is in good agreement with $\tilde{\omega}^2$ calculated for the other members of the series, the mean of which is $98.5\times10^4$.

The frequency shift $\Delta\tilde{\nu}=794$ cm$^{-1}$ observed by Kohlrausch and Barnes did not appear on any of the plates obtained by the author, using tetramethylmethane as the scatterer, although much weaker lines were observed than K. and B. were able to observe. It seems extremely probable that this line is due to isobutane since the strongest line in the isobutane spectrum corresponds to this line within experimental error and isobutane is one of the principal impurities in tetramethylmethane and certainly one of the most difficult to remove.

TABLE I. *Frequency shifts cm$^{-1}$.*

| Tetramethyl-methane | Tetramethyl-methane | Tetramethyl-methane chloride | *n*-amyl chloride | *n*-amyl chloride |
|---|---|---|---|---|
| Kohlrausch and Barnes | Rank | Rank | Harkins and Haun | Rank |
| | | 123 (5) | | 268 (6) |
| | | 210 (4) | | 286 (2B)* |
| | | 321 (10) | | 349 (4) |
| 332 (1) | 336 (10) | 333 (3) | | 402 (3) |
| | 415 (3) | 399 (3) | 454 (1) | 460 (2) |
| | | 412 (3) | 658 (10) | 657 (20) |
| | | 471 (5) | | 685 (3) |
| 732 (5) | 734 (20) | 722 (20) | 730 (8) | 726 (10) |
| 794 (2) | | 757 (5) | | Band 726 to |
| | | 883 (2) | | 782 (3)* |
| | | 907 (5) | | 793 (4) |
| 920 (3a) | 925 (15B) | 938 (4) | | 822 (3B) |
| | | 1025 (3) | | 843 (4) |
| | | 1144 (4) | | 881 (3B) |
| | | 1199 (4) | 893 (1) | 898 (5) |
| 1241 (2a) | 1253 (20B) | 1258 (4) | | 929 (2)* |
| | | 1284 (5B) | 970 (1) | 981 (3B)* |
| 1448 (4a) | 1456 (15) | 1451 (10) | | 1034 (3) |
| | | 1467 (5) | | 1067 (10) |
| | | | | 1097 (4B) |
| | | | | 1114 (4B) |
| | | | | 1177 (1B)* |
| | | | | 1234 (1B) |
| | | | | 1284 (3B) |
| | | | | 1307 (8) |
| | | | 1450 (10) | 1452 (20B) |
| | 2713 (5) | 2722 (3) | 2877 (8) | 2871 (20V.B.) |
| | 2746 (3) | 2872 (7B) | 2911 (2) | 2908 (20V.B.) |
| 2792 (2a) | 2794 (3) | 2910 (10) | 2941 (4) | 2939 (20V.B.) |
| 2866 (5) | 2865 (7) | 2929 (3) | 2967 (4) | 2964 (20V.B.) |
| 2892 (2) | 2893 (5) | 2946 (8) | | 3005 (3) |
| 2908 (6) | 2913 (10) | Band 2954 | | |
| | 2938 (3) | to 2996 | | |
| 2954 (5a) | 2957 (7B) | | | |

## *N*-AMYL CHLORIDE AND TETRAMETHYLMETHANE CHLORIDE

Fig. 1, B, is a reproduction of the spectrum of tetramethylmethane chloride, while D is the same spectrum more highly enlarged in order to show several of the close doublets. Fig. 1, C, is a reproduction of the spectrum of *n*-amyl chloride.

The Raman spectrum of *n*-amyl chloride has been obtained by Harkins and Haun[7] without the use of filters. Their results appear in Table I as well as the results obtained in the present investigation.

The spectrum of tetramethylmethane chloride was obtained for the first time. The spectrum of

[7] Harkins and Haun, J. Am. Chem. Soc. **54**, 3920 (1932).

this compound contrasted with that of tetramethylmethane shows in a striking manner the removal of the degeneracy of an extremely symmetrical molecule by partially destroying its symmetrical character. However, it seems difficult to attempt to assign this splitting to certain definite vibrations of the atoms in the molecule until more experimental work is available on a series of derivatives of tetramethylmethane, which work is now in progress.

The author wishes to express his appreciation to Dr. F. C. Whitmore of the Chemistry Department for making the compounds available which were used in the present investigation.

# Mathematical Methods for Computing Thermodynamic Functions from Spectroscopic Data*

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Methods of summation are given for the $Q$-sum, and the related sums which are needed in calculating free energies, entropies and heat capacities from spectroscopic data. All necessary formulas are presented for the treatment of a linear molecule with arbitrary orbital angular momentum, spin multiplicity and nuclear symmetry. The nonlinear molecule is much more difficult; necessary formulas are given for the special case of a $^1\Sigma$ molecule with two equal principal moments of inertia. The application of these methods is illustrated by the calculation of the entropy, heat content and heat capacity of carbon monoxide from 50 to 5000°K.

## INTRODUCTION

WHENEVER the energy levels and quantum weights for a substance are known, it is possible to calculate its specific heat and entropy and other thermodynamic functions such as $F^0-E_0^0$ which do not involve heats of reaction.[1, 2, 3, 4] At present this type of calculation is restricted to gases at pressures where they may be considered perfect. When the internal energy may be represented as that of a rigid rotator, plus one or more harmonic oscillators, the calculations are comparatively easy. When greater accuracy is needed than this approximation permits, the calculations become very laborious unless full advantage is taken of analytic methods of summation. It is the purpose of this paper to develop these methods more fully than has been done previously.

The fundamental summation is

$$Q=\sum_i p_i e^{-\epsilon_i/kT}. \tag{1}$$

In terms of $Q$,

$$F/T=-R\log Q, \tag{2}$$

$$H=-[R/Q][dQ/d(1/T)], \tag{3}$$

$$C_P=(R/T^2)\{d^2Q/Qd(1/T)^2 - [dQ/Qd(1/T)]^2\}. \tag{4}$$

In previous treatments of this problem, since $Q$ is obtained by numerical summation, it has been necessary to sum also

$$P=\sum_i \epsilon_i p_i e^{-\epsilon_i/kT}=-k^{-1}dQ/d(1/T) \tag{5}$$

and

$$N=\sum_i \epsilon_i^2 p_i e^{-\epsilon_i/kT}=k^{-2}d^2Q/d(1/T)^2. \tag{6}$$

The methods described here, however, lead to an analytic expression for $Q$ from which the derivatives may be obtained directly. We do not avoid having to do three summations to get the specific heat; the work of setting up the sum, however, need be done only once. This is the most difficult part of the calculation; the rest is pure routine and could be entrusted to even an unskilled computer.

The energy levels are usually written as

$$\epsilon=\epsilon_e+\epsilon_{e,\,v}+\epsilon_{e,\,v,\,r}, \tag{7}$$

where $e$, $v$ and $r$ refer to the electronic, vibrational and rotational quantum numbers. The number of different electron states which contribute appreciably to $Q$ is always small, and we simply evaluate the sums separately for each state and add the results. We shall therefore omit the subscript $e$ from here on. The exact form of $\epsilon_{v,\,r}$ is of importance. For a diatomic molecule, theory predicts, and experiment confirms, that

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† Associate physical chemist.

[1] Hicks and Mitchell, J. Am. Chem. Soc. **48**, 1520 (1926).

[2] Hutchisson, J. Am. Chem. Soc. **50**, 1895 (1928).

[3] Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

[4] Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

$$\epsilon_{v,r}=B_vK(K+1)+D_vK^2(K+1)^2+\cdots, \quad (8)$$

where

$$B_v=B_0+\alpha v+\beta v^2+\cdots, \quad (9)$$

$$D_v=D_0+\gamma v+\delta v^2+\cdots. \quad (10)$$

For all moderate values of the quantum numbers, the first term in each expansion is by far the largest. If, then, an analytic formula can be found for the sum with respect to $K$, the result can be expanded as a power series in $v$. The procedure to be used in summing over $v$, when this has been done, has already been described.[5] It is thus only necessary to treat the rotational sums.

## Methods of Summation

For a $^1\Sigma$ molecule with unlike atoms and, therefore, evenly weighted rotational levels and with $D_v$ and higher coefficients all zero, Mulholland[6] has derived the asymptotic expansion

$$Q=\sum_{K=0}^{\infty}(2K+1)e^{-BK(K+1)} \quad (11)$$
$$=e^{B/4}\left[\frac{1}{B}+\sum_{n=0}^{k}B_{n+1}(1-2^{-2n-1})B^n/(n+1)!+R_k\right],$$

where $B_1=1/6$, $B_2=1/30$, $B_3=1/42$, $B_4=1/30$, $B_5=5/66$, $B_6=691/2730$, $B_7=7/6$ $\cdots$ are the Bernoulli numbers.

Giauque and Overstreet[7] pointed out that the exponential terms in $D_v$, etc., can be expanded as a power series and the resulting expression summed term by term. They state that for these correction terms it is sufficiently accurate to replace sums by integrals. This is, in fact, correct for most purposes but it appears worth while to have the more exact formulas.

Mulholland's result (11) was first derived by using the theory of residues. Recently Miss Viney[8] has pointed out that the summation is made much more readily by the use of the Euler-Maclaurin expansion formula. This method has been used to derive the fundamental sums of the following sections; the others have been obtained by repeated differentiation with respect to $B$.

In writing the results, we use, throughout, the notation

$$E=e^{-BK(K+1)} \quad (12)$$

and in indicating the range of summation we write

$$K/2=L, \quad K/2-\tfrac{1}{2}=M, \quad K-\tfrac{1}{2}=N,$$
$$K/2-\tfrac{1}{4}=P, \quad K/2-\tfrac{3}{4}=R. \quad (13)$$

## Linear Molecules

### Integral K

$$\sum_{K=0}^{\infty}(2K+1)^{2n+1}E=e^{B/4}\left[2^{2n}n!B^{-n-1}+(-1)^n\sum_{k=0}^{\lambda}(2^{2n+2k+1}-1)B_{n+k+1}B^k/2^{2k+1}(n+k+1)k!+R_\lambda\right] \quad (14)$$

$$\sum_{L=0}^{\infty}(2K+1)^{2n+1}E=(\tfrac{1}{2})\sum_{K=0}^{\infty}(2K+1)^{2n+1}E, \quad (15)$$

$$\sum_{M=0}^{\infty}(2K+1)^{2n+1}E=(\tfrac{1}{2})\sum_{K=0}^{\infty}(2K+1)^{2n+1}E. \quad (16)$$

(15) and (16) are exact relations between the asymptotic expansions of the summations, but not between the summations themselves. Thus, as $B$ approaches $\infty$, the sums over $K$ and $L$ approach 1, while that over $M$ approaches 0; the asymptotic expansions all approach $\infty$, thus failing completely. For the small values of $B$ for which the expansions are intended, however, (15) and (16) hold to a very high order of accuracy. It may be noted in (18) that similar relations do not always hold.

[5] Kassel, Phys. Rev. **43**, 364 (1933). The discussion of the unavoidable error given here assumes replacement of sums by integrals.

[6] Mulholland, Proc. Cambridge Phil. Soc. **24**, 280 (1928).

[7] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[8] Miss Viney, Proc. Cambridge Phil. Soc. **29**, 142 (1933).

$$\sum_{K=0}^{\infty}(2K+1)^{2n}E=[\tfrac{1}{2}][(2n)!/n!]\pi^{\frac{1}{2}}e^{B/4}B^{-n-\frac{1}{2}}, \tag{17}$$

$$\sum_{L=0}^{\infty}(2K+1)^{2n}E=(\tfrac{1}{2})\sum_{K=0}^{\infty}(2K+1)^{2n}E+(-1)^n\sum_{k=0}^{\lambda}E_{n+k}B^k/2^{2k+2}k!+R_\lambda. \tag{18}$$

A similar expression holds for the sum over $M$, with the opposite sign before the second term on the right. Here $E_1=1$, $E_2=5$, $E_3=61$, $E_4=1385$, $E_5=50{,}521$, $E_6=2{,}702{,}765$, etc., are Euler's numbers.

The foregoing formulas will be used when the energy is written in terms of $K+\frac{1}{2}$. When it is given in powers of $K(K+1)$, we may either transform directly to powers of $K+\frac{1}{2}$ or use the following formulas:

$$\sum_{K=0}^{\infty}K^n(K+1)^n(2K+1)E=n!B^{-n-1}+(-1)^n[B^{-n}/3(-n)!+B^{1-n}/15(1-n)!+8B^{2-n}/315(2-n)!$$
$$+2B^{3-n}/105(3-n)!+32B^{4-n}/1155(4-n)!+\cdots]. \tag{19}$$

For the purposes of this equation, we take $0!=1$, and $n!=\infty$ when $n$ is negative.

$$\sum_{L=0}^{\infty}K^n(K+1)^n(2K+1)E=\sum_{M=0}^{\infty}K^n(K+1)^n(2K+1)E=(\tfrac{1}{2})\sum_{K=0}^{\infty}K^n(K+1)^n(2K+1)E. \tag{20}$$

With the preceding formulas we can treat any $^1\Sigma$ molecule. To avoid this restriction we must be able to carry out our summations when the quantum weight is not $2K+1$, when one or more of the lowest $K$ values is absent and when $K$ is half-integral. We shall treat these difficulties in the order given. The first arises, for example, with oxygen for which the quantum weights of the $F_1$, $F_2$ and $F_3$ components of the normal state are $2K+3$, $2K+1$ and $2K-1$, respectively. When the energy is written in terms of $K+\frac{1}{2}$, Eqs. (14)–(18) are sufficient; thus

$$\sum_{K=0}^{\infty}(2K+1)^5(2K-1)E=\sum_{K=0}^{\infty}(2K+1)^6E-2\sum_{K=0}^{\infty}(2K+1)^5E.$$

The following two equations permit similar combinations when $K(K+1)$ is used.

$$\sum_{K=0}^{\infty}K^n(K+1)^nE=2^{-2n-1}\pi^{\frac{1}{2}}e^{B/4}\sum_{k=0}^{n}(-1)^k[(2n-2k)!/(n-k)!]\binom{n}{k}B^{-n+k-\frac{1}{2}}, \tag{21}$$

$$\sum_{L=0}^{\infty}K^n(K+1)^nE=(\tfrac{1}{2})\sum_{K=0}^{\infty}K^n(K+1)^nE+(-1)^n[B^{-n}/4(-n)!+B^{1-n}/8(1-n)!+B^{2-n}/8(2-n)!$$
$$+5B^{3-n}/16(3-n)!+13B^{4-n}/8(4-n)!+\cdots]. \tag{22}$$

This equation is subject to the same conventions as (19) concerning the treatment of factorials.

When some of the lower values of $K$ are absent, the preceding formulas are readily altered. Thus, to adapt (19) to a situation in which the lowest term is at $K=2$, we have to diminish the fundamental $Q$-sum by $1+3e^{-2B}$. By expanding the exponential term and differentiating repeatedly, it is found that (19) must be diminished by $4B^{-n}/(-n)!-6B^{1-n}/(1-n)!+12B^{2-n}/(2-n)!-24B^{3-n}/(3-n)!$ $+48B^{4-n}/(4-n)!+\cdots$. It should be noted that these terms combine with those already present so that the new expansion is no more complex than the original one. Of course, it is not necessary to treat the problem in this way; the extraneous terms may be simply subtracted as such.

**Half-integral K**

In this section we remove the last of the restrictions mentioned above, making possible the exact treatment of any linear molecule.

$$\sum_{N=0}^{\infty}(2K+1)^{2n+1}E=2^{2n}e^{B/4}[n!B^{-n-1}+(-1)^{n+1}\sum_{k=0}^{\lambda}B_{n+k+1}B^k/(n+k+1)k!+R_\lambda]. \tag{23}$$

Sutherland[9] has previously derived (23) for $n=0$, using a method similar to that of Mulholland; the signs of the even-numbered terms in his result are incorrect, however, because of a confusion between various nomenclatures for the Bernoulli numbers.

$$\sum_{P=0}^{\infty}(2K+1)^{2n+1}E=2^{2n}e^{B/4}[n!B^{-n-1}/2+(-1)^{n}\sum_{k=0}^{\lambda}(2^{2n+2k+1}-1)B_{n+k+1}B^k/(n+k+1)k!+R_\lambda], \tag{24}$$

$$\sum_{R=0}^{\infty}(2K+1)^{2n+1}E=2^{2n}e^{B/4}[n!B^{-n-1}/2+(-1)^{n+1}\sum_{k=0}^{\infty}2^{2n+2k+1}B_{n+k+1}B^k/(n+k+1)k!+R_\lambda], \tag{25}$$

$$\sum_{N=0}^{\infty}(2K+1)^{2n}E=\sum_{K=0}^{\infty}(2K+1)^{2n}E-e^{B/4}/2(-n)!, \tag{26}$$

$$\sum_{P=0}^{\infty}(2K+1)^{2n}E=(1/2)\sum_{K=0}^{\infty}(2K+1)^{2n}E, \tag{27}$$

$$\sum_{N=0}^{\infty}K^n(K+1)^n(2K+1)E=n!B^{-n-1}+(-1)^{n+1}[-B^{-n}/12(-n)!+13B^{1-n}/480(1-n)!$$
$$+433B^{2-n}/20{,}160(2-n)!+2047B^{3-n}/107{,}520(3-n)!+33{,}067B^{4-n}/1{,}182{,}720(4-n)!+\cdots], \tag{28}$$

$$\sum_{P=0}^{\infty}K^n(K+1)^n(2K+1)E=n!B^{-n-1}/2+(-1)^{n}[7B^{-n}/24(-n)!+167B^{1-n}/960(1-n)!$$
$$+12{,}797B^{2-n}/40{,}320(2-n)!+272{,}633B^{3-n}/215{,}040(3-n)!$$
$$+21{,}054{,}923B^{4-n}/2{,}365{,}440(4-n)!+\cdots], \tag{29}$$

$$\sum_{R=0}^{\infty}K^n(K+1)^n(2K+1)E=n!B^{-n-1}/2+(-1)^{n+1}[5B^{-n}/24(-n)!+193B^{1-n}/960(1-n)!$$
$$+13{,}663B^{2-n}/40{,}320(2-n)!+276{,}727B^{3-n}/215{,}040(3-n)!$$
$$+21{,}121{,}057B^{4-n}/2{,}365{,}440(4-n)!+\cdots], \tag{30}$$

$$\sum_{N=0}^{\infty}K^n(K+1)^nE=\sum_{K=0}^{\infty}K^n(K+1)^nE+(-1)^{n+1}2^{-2n-1}e^{B/4}, \tag{31}$$

$$\sum_{P=0}^{\infty}K^n(K+1)^nE=(\tfrac{1}{2})\sum_{K=0}^{\infty}K^n(K+1)^nE. \tag{32}$$

**Accuracy**

These formulas complete the list necessary for the discussion of any linear molecule. There is naturally some individual variation, but in general they are useful for values of $B\leqq 0.5$. This is shown by the following comparison for $B=0.5$. (See Table I.)

[9] Sutherland, Proc. Cambridge Phil. Soc. **26**, 402 (1930).

TABLE I.

| | Direct summation | Asymptotic expansion |
|---|---|---|
| $K$ | $(2K+1)e^{-K(K+1)}$ | |
| 0 | 1.000 000 000 | $1/B=$ 2.000 000 000 |
| 1 | 1.103 638 323 | $1/3=$ .333 333 333 |
| 2 | .248 935 342 | $B/15=$ .033 333 333 |
| 3 | .017 351 265 | $4B^2/315=$ .003 174 603 |
| 4 | .000 408 600 | $B^3/315=$ .000 396 825 |
| 5 | .000 003 365 | $4B^4/3465=$ .000 072 150 |
| 6 | .000 000 010 | |
| | 2.370 336 905 | 2.370 314 244 |

The error of the calculation from the asymptotic expansion is 11 parts per million, corresponding to 0.000022 cal./deg. in $F/T$; even this quite negligible error is due in large part to the omission of the $B^5$ term in the expansion. At higher temperatures and correspondingly smaller $B$ values, the error of the asymptotic expansion is even less.

## NONLINEAR MOLECULES. SYMMETRICAL TOP TYPE

Our knowledge of polyatomic molecules is relatively very meager. The energy levels of a rigid rotator with moments of inertia $A$, $A$ and $C$ are known to be

$$K(K+1)\sigma-n^2\beta\sigma \qquad |n|\leqq K,$$

where $\sigma=h^2/8\pi^2A$ and $\beta=A/C-1$. The weight of the level defined by $K$ and $n$ is $(2K+1)$ if we permit both positive and negative $n$. The levels of $^1\Sigma$ molecules are presumably given by such a formula, with suitable stretching and interaction terms.

The method to be used in applying the Euler-Maclaurin summation formula to the calculation of an asymptotic expansion for the $Q$-sum for this case has been given by Miss Viney[10]; her result is

$$S(1)=\pi^{\frac{1}{2}}\sigma^{-1}\alpha^{-\frac{1}{2}}[1+(\sigma/\alpha)(\sigma/4+\tau/3)+(\sigma/\alpha)^2(\sigma^2/32+\sigma\tau/15+\tau^2/12)$$
$$+(\sigma/\alpha)^3(\sigma^3/384+\sigma^2\tau/96+\sigma\tau^2/60+4\tau^3/315)+\cdots],$$

where

$$S(x)=\sum_{K=0}^{\infty}\sum_{|n|=-K}^{\infty}(2K+1)xe^{-K(K+1)\sigma-\beta\sigma n^2} \tag{33}$$

and, in the present notation,

$$\tau=\beta\sigma, \qquad \alpha=\sigma+\tau=(\beta+1)\sigma.$$

Repetition of her calculations shows that the coefficient of $(\sigma/\alpha)^2$ should be[11]

$$\sigma^2/32+\sigma\tau/12+\tau^2/15.$$

[10] Miss Viney, reference 8.

[11] Just after Miss Viney's paper appeared, the present writer completed a numerical determination of the form of $S(1)$ out to and including the third term, the result of which was exactly correct. It appears possible that a similar method may be useful in other cases where an analytic treatment is difficult. In the present case, the sums were evaluated for $\sigma=0.005$, 0.01 and 0.02, with various values of $\beta\sigma$ from 0 to 0.50; the parameters were chosen such that the exponential factors could be found as powers, using a calculating machine. Once a suitable technique for the calculations has been worked out, they are surprisingly rapid; there is no doubt that the higher terms of (80) could be obtained in this way more rapidly than by Miss Viney's method, provided one is willing to check such a coefficient as 511/811,008 to perhaps 0.1 percent and guess its exact value. It may also be well to mention that, according to a private communication from Miss Viney, the error in her result was made in the final stage of the computation where it would not affect the following term.

The laborious calculations necessary to check the last term have not been made. The corrected result can be put into the much simpler form,

$$S(1)=\pi^{1/2}\sigma^{-3/2}e^{\sigma/4}(\beta+1)^{-1/2}[1+(1/12)\beta(\beta+1)^{-1}\sigma+(7/480)\beta^2(\beta+1)^{-2}\sigma^2+(31/8064)\beta^3(\beta+1)^{-3}\sigma^3$$
$$+(127/92{,}160)\beta^4(\beta+1)^{-4}\sigma^4+(511/811{,}008)\beta^5(\beta+1)^{-5}\sigma^5+\cdots], \quad (34)$$

where the last two terms have been added by conjecture in comparison with (24). From this form we easily derive the leading terms of the rotational heat capacity

$$C_{\text{rot}}/R=\sigma^2 d^2 \log S(1)/d\sigma^2$$
$$=(3/2)+(1/45)\beta^2(\beta+1)^{-2}\sigma^2+\cdots.$$

Formulas of this type have a very limited use since the correction terms because of stretching are usually too large to be neglected. This result is given to correct an error in Miss Viney's paper.

By suitable differentiations of (34) with respect to $\sigma$ and $\beta$ we obtain

$$S(n^2)=(1/2)\pi^{1/2}\sigma^{-5/2}e^{\sigma/4}(\beta+1)^{-3/2}[1+(1/12)(\beta-2)(\beta+1)^{-1}\sigma+(7/480)(\beta^2-4\beta)(\beta+1)^{-2}\sigma^2$$
$$+(31/8064)(\beta^3-6\beta^2)(\beta+1)^{-3}\sigma^3+(127/92{,}160)(\beta^4-8\beta^3)(\beta+1)^{-4}\sigma^4$$
$$+(511/811{,}008)(\beta^5-10\beta^4)(\beta+1)^{-5}\sigma^5+\cdots], \quad (35)$$

$$S[K(K+1)]=\pi^{1/2}\sigma^{-5/2}e^{\sigma/4}(\beta+1)^{-1/2}[(1/2)(2\beta+3)(\beta+1)^{-1}-(1/8)(2\beta^2+3\beta+2)(\beta+1)^{-2}\sigma$$
$$-(1/960)(34\beta^3+19\beta^2+20\beta)(\beta+1)^{-3}\sigma^2-(1/80{,}640)(914\beta^4+123\beta^3+294\beta^2)(\beta+1)^{-4}\sigma^3$$
$$-(1/1{,}290{,}240)(6574\beta^5-187\beta^4+1240\beta^3)(\beta+1)^{-5}\sigma^4$$
$$-(1/8{,}110{,}080)(23{,}234\beta^6-2077\beta^5+2794\beta^4)(\beta+1)^{-6}\sigma^5-\cdots], \quad (36)$$

$$S(n^4)=(1/4)\pi^{1/2}\sigma^{-7/2}e^{\sigma/4}(\beta+1)^{-5/2}[3+(1/12)(3\beta-12)(\beta+1)^{-1}\sigma+(7/480)(3\beta^2-24\beta+8)(\beta+1)^{-2}\sigma^2$$
$$+(31/8064)(3\beta^3-36\beta^2+24\beta)(\beta+1)^{-3}\sigma^3+(127/92{,}160)(3\beta^4-48\beta^3+48\beta^2)(\beta+1)^{-4}\sigma^4$$
$$+(511/811{,}008)(3\beta^5-60\beta^4+80\beta^3)(\beta+1)^{-5}\sigma^5+\cdots], \quad (37)$$

$$S[n^2K(K+1)]=(1/4)\pi^{1/2}\sigma^{-7/2}e^{\sigma/4}(\beta+1)^{-3/2}[(2\beta+5)(\beta+1)^{-1}-(1/4)(2\beta^2+\beta+4)(\beta+1)^{-2}\sigma$$
$$-(1/480)(34\beta^3-147\beta^2+24\beta-40)(\beta+1)^{-3}\sigma^2$$
$$-(1/40{,}320)(914\beta^4-6943\beta^3+732\beta^2-1176\beta)(\beta+1)^{-4}\sigma^3$$
$$-(1/645{,}120)(6574\beta^5-66{,}301\beta^4+7696\beta^3-7440\beta^2)(\beta+1)^{-5}\sigma^4$$
$$-(1/4{,}055{,}040)(23{,}234\beta^6-285{,}039\beta^5+34{,}740\beta^4-22{,}352\beta^3)(\beta+1)^{-6}\sigma^5-\cdots], \quad (38)$$

$$S[K^2(K+1)^2]=(1/4)\pi^{1/2}\sigma^{-7/2}e^{\sigma/4}(\beta+1)^{-1/2}[(8\beta^2+20\beta+15)(\beta+1)^{-2}$$
$$-(1/4)(8\beta^3+28\beta^2+27\beta+12)(\beta+1)^{-3}\sigma+(1/480)(120\beta^4+220\beta^3+585\beta^2+360\beta+120)(\beta+1)^{-4}\sigma^2$$
$$+(1/40{,}320)(3256\beta^5-2252\beta^4+5013\beta^3+1596\beta^2+840\beta)(\beta+1)^{-5}\sigma^3$$
$$+(1/645{,}120)(33{,}608\beta^6-31{,}532\beta^5+22{,}487\beta^4+1968\beta^3+2352\beta^2)(\beta+1)^{-6}\sigma^4$$
$$+(1/28{,}385{,}280)(1{,}120{,}456\beta^7-969{,}636\beta^6+431\,955\beta^5-8228\beta^4+27{,}280\beta^3)(\beta+1)^{-7}\sigma^5+\cdots], \quad (39)$$

$$S(n^6)=(3/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-7/2}[5+(1/12)(5\beta-30)(\beta+1)^{-1}\sigma+(7/480)(5\beta^2-60\beta+40)(\beta+1)^{-2}\sigma^2$$
$$+(31/8064)(5\beta^3-90\beta^2+120\beta-16)(\beta+1)^{-3}\sigma^3$$
$$+(127/92,160)(5\beta^4-120\beta^3+240\beta^2-64\beta)(\beta+1)^{-4}\sigma^4$$
$$+(511/811,008)(5\beta^5-150\beta^4+400\beta^3-160\beta^2)(\beta+1)^{-5}\sigma^5+\cdots], \quad (40)$$

$$S[n^4K(K+1)]=(1/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-5/2}[(6\beta+21)(\beta+1)^{-1}-(1/4)(6\beta^2-3\beta+26)(\beta+1)^{-2}\sigma$$
$$-(1/160)(34\beta^3-313\beta^2+252\beta-136)(\beta+1)^{-3}\sigma^2$$
$$-(1/13,440)(914\beta^4-14,009\beta^3+15,594\beta^2-4504\beta+784)(\beta+1)^{-4}\sigma^3$$
$$-(1/215,040)(6574\beta^5-132,415\beta^4+194,760\beta^3-37,712\beta^2+9920\beta)(\beta+1)^{-5}\sigma^4$$
$$-(1/1,351,680)(23,234\beta^6-568,001\beta^5$$
$$+1,031,190\beta^4-159,696\beta^3+44,704\beta^2)(\beta+1)^{-6}\sigma^5-\cdots] \quad (41)$$

$$S[n^2K^2(K+1)^2]=(1/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-3/2}[(8\beta^2+28\beta+35)(\beta+1)^{-2}$$
$$-(1/4)(8\beta^3+36\beta^2+23\beta+30)(\beta+1)^{-3}\sigma+(1/160)(40\beta^4-100\beta^3+535\beta^2+60\beta+120)(\beta+1)^{-4}\sigma^2$$
$$+(1/40,320)(3256\beta^5-39,316\beta^4+43,081\beta^3-18,906\beta^2+1176\beta-1680)(\beta+1)^{-5}\sigma^3$$
$$+(1/645,120)(33,608\beta^6-497,892\beta^5+427,755\beta^4-166,120\beta^3+9360\beta^2-9408\beta)(\beta+1)^{-6}\sigma^4$$
$$+(1/28,385,280)(1,120,456\beta^7-18,595,292\beta^6+13,795,407\beta^5-4,377,146\beta^4+311,344\beta^3$$
$$-163,680\beta^2)(\beta+1)^{-7}\sigma^5+\cdots], \quad (42)$$

$$S[K^3(K+1)^3]=(1/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-1/2}[(48\beta^3+168\beta^2+210\beta+105)(\beta+1)^{-3}$$
$$-(1/4)(48\beta^4+216\beta^3+378\beta^2+265\beta+90)(\beta+1)^{-4}\sigma$$
$$+(1/32)(48\beta^5+264\beta^4+418\beta^3+553\beta^2+276\beta+72)(\beta+1)^{-5}\sigma^2$$
$$-(1/384)(48\beta^6-200\beta^5+842\beta^4+457\beta^3+558\beta^2+216\beta+48)(\beta+1)^{-6}\sigma^3$$
$$-(1/215,040)(31,088\beta^7-153,912\beta^6+149,610\beta^5-22,235\beta^4+28,680\beta^3+6384\beta^2+2240\beta)(\beta+1)^{-7}\sigma^4$$
$$-(1/9,461,760)(1,740,400\beta^8-5,785,928\beta^7+4,009,682\beta^6-922,315\beta^5+333,850\beta^4+21,648\beta^3$$
$$+17,248\beta^2)(\beta+1)^{-8}\sigma^5+\cdots] \quad (43)$$

$$S(n^8)=(3/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-9/2}[35+(1/12)(35\beta-280)(\beta+1)^{-1}\sigma$$
$$+(7/480)(35\beta^2-560\beta+560)(\beta+1)^{-2}\sigma^2+(31/8064)(35\beta^3-840\beta^2+1680\beta-448)(\beta+1)^{-3}\sigma^3$$
$$+(127/92,160)(35\beta^4-1120\beta^3+3360\beta^2-1792\beta+128)(\beta+1)^{-4}\sigma^4$$
$$+(511/811,008)(35\beta^5-1400\beta^4+5600\beta^3-4480\beta^2+640\beta)(\beta+1)^{-5}\sigma^5+\cdots], \quad (44)$$

$$S[n^6K(K+1)]=(1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-7/2}[(30\beta+135)(\beta+1)^{-1}$$
$$-(1/4)(30\beta^2-45\beta+240)(\beta+1)^{-2}\sigma-(1/160)(170\beta^3-2395\beta^2+3520\beta-2000)(\beta+1)^{-3}\sigma^2$$
$$-(1/13440)(4570\beta^4-105,375\beta^3+224,400\beta^2-111,920\beta+19,200)(\beta+1)^{-4}\sigma^3$$
$$-(1/215,040)(32,870\beta^5-992,645\beta^4+2,812,160\beta^3-1,583,392\beta^2+279,808\beta-19,840)(\beta+1)^{-5}\sigma^4$$
$$-(1/1,351,680)(116,170\beta^6-4,254,815\beta^5+14,960,720\beta^4-10,006,176\beta^3+1,539,328\beta^2$$
$$-178,816\beta)(\beta+1)^{-6}\sigma^5-\cdots], \quad (45)$$

$$S[n^4K^2(K+1)^2]=(1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-5/2}[(24\beta^2+108\beta+189)(\beta+1)^{-2}$$
$$-(1/4)(24\beta^3+132\beta^2+17\beta+224)(\beta+1)^{-3}\sigma$$
$$+(1/160)(120\beta^4-820\beta^3+4345\beta^2-1600\beta+1200)(\beta+1)^{-4}\sigma^2$$
$$+(1/13{,}440)(3256\beta^5-76{,}380\beta^4+205{,}365\beta^3-142{,}880\beta^2+29{,}520\beta-8064)(\beta+1)^{-5}\sigma^3$$
$$+(1/215{,}040)(33{,}608\beta^6-964{,}252\beta^5+2{,}657{,}735\beta^4-1{,}639{,}040\beta^3+366{,}560\beta^2-53{,}248\beta+6272)$$
$$\times(\beta+1)^{-6}\sigma^4+(1/9{,}461{,}760)(1{,}120{,}456\beta^7-36{,}220{,}948\beta^6+106{,}570{,}451\beta^5-59{,}116{,}128\beta^4$$
$$+12{,}813{,}984\beta^3-1{,}331{,}968\beta^2+218{,}240\beta)(\beta+1)^{-7}\sigma^5+\cdots], \quad (46)$$

$$S[n^2K^3(K+1)^3]=(1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-3/2}[(48\beta^3+216\beta^2+378\beta+315)(\beta+1)^{-3}$$
$$-(1/4)(48\beta^4+264\beta^3+594\beta^2+343\beta+280)(\beta+1)^{-4}\sigma$$
$$+(1/32)(48\beta^5+312\beta^4-22\beta^3+1363\beta^2+272\beta+240)(\beta+1)^{-5}\sigma^2$$
$$-(1/128)(16\beta^6-392\beta^5+2070\beta^4-1179\beta^3+760\beta^2+48\beta+64)(\beta+1)^{-6}\sigma^3$$
$$-(1/215{,}040)(31{,}088\beta^7-896{,}968\beta^6+2{,}594{,}994\beta^5-1{,}651{,}745\beta^4+436{,}000\beta^3-101{,}856\beta^2$$
$$+3584\beta-4480)(\beta+1)^{-7}\sigma^4-(1/9{,}461{,}760)(1{,}740{,}400\beta^8-45{,}204{,}184\beta^7+101{,}051{,}402\beta^6$$
$$-54{,}572{,}389\beta^5+12{,}227{,}800\beta^4-2{,}432{,}672\beta^3+94{,}336\beta^2-68{,}992\beta)(\beta+1)^{-8}\sigma^5-\cdots], \quad (47)$$

$$S[K^4(K+1)^4]=(1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-1/2}[(384\beta^4+1728\beta^3+3024\beta^2+2520\beta+945)(\beta+1)^{-4}$$
$$-(1/4)(384\beta^5+2112\beta^4+4752\beta^3+5544\beta^2+3045\beta+840)(\beta+1)^{-5}\sigma$$
$$+(1/32)(384\beta^6+2496\beta^5+6864\beta^4+8440\beta^3+7865\beta^2+3280\beta+720)(\beta+1)^{-6}\sigma^2$$
$$-(1/384)(384\beta^7+2880\beta^6+1680\beta^5+17{,}352\beta^4+11{,}565\beta^3+9240\beta^2+3120\beta+576)(\beta+1)^{-7}\sigma^3$$
$$+(1/30{,}720)(1920\beta^8-11{,}752\beta^7+390{,}928\beta^6-176{,}520\beta^5+153{,}925\beta^4+52{,}000\beta^3+40{,}800\beta^2$$
$$+11{,}520\beta+1920)(\beta+1)^{-8}\sigma^4+(1/9{,}461{,}760)(4{,}164{,}736\beta^9-51{,}267{,}904\beta^8+96{,}478{,}384\beta^7$$
$$-48{,}777{,}416\beta^6+14{,}583{,}375\beta^5-1{,}163{,}976\beta^4+1{,}094{,}368\beta^3+187{,}264\beta^2+49{,}280\beta)(\beta+1)^{-9}\sigma^5$$
$$+\cdots]. \quad (48)$$

In deriving (35) to (48), all possible orders of differentiation were used; there was thus no chance for an error to escape detection. As a further check, the entire calculation was repeated for the special case $\beta=1$ and the resulting equations checked by comparison with those obtained by substituting $\beta=1$ in (35) to (48); exact agreement was found in every case.

## Application to Carbon Monoxide

The free energy of carbon monoxide has been calculated[12] but the entropy, heat content and heat capacity have not been given. We shall therefore calculate these values to illustrate the convenience of the proposed methods. We use the spectroscopic data given by Clayton and Giauque, correcting the rather obvious misprint in the sign of $\alpha$. We use $R=1.9869$ cal./mol, $hc/k=1.432{,}500$ cm(°K) and 7.267 for the numerical constant of the free energy equation. It may be worth while to point out that several different values of $hc/k$ may be derived from the *International Critical Tables* which should therefore not be cited as the source of the value used in any exact calculation.

The energy may be written

[12] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

$$hc\epsilon/kT=(0.00264010/\tau)(1-0.0108519v)K(K+1)+(7.711{,}73\times10^{-9}/\tau)(1-0.012{,}850{,}6v)(K+1/2)^4$$
$$+3.086{,}60v/\tau-0.018{,}192{,}7v^2/\tau, \quad \text{with} \quad \tau=T/1000.$$

We now calculate $Q_r(v)$, the rotational $Q$-sum regarded as a function of $v$. To do this, we expand

$$\exp[-(7.711{,}73\times10^{-9}/\tau)(1-0.012{,}850{,}6v)(K+1/2)^4]$$

as a power series, using the first four terms. Then, using (14), we can immediately write down $Q_r(v)$. After making a few power series expansions in $v$ and rearranging a little, the result is

$$Q_r(v)=378.774\tau[0.999{,}999+0.000{,}880/\tau+4.65\times10^{-7}/\tau^2-2.2128\times10^{-3}\tau+1.469\times10^{-5}\tau^2$$
$$-1.625\times10^{-7}\tau^3+v(0.010{,}851{,}9-5.042\times10^{-9}/\tau^2-4.360\times10^{-5}\tau+4.19\times10^{-7}\tau^2-6.0\times10^{-9}\tau^3)$$
$$+v^2(1.178\times10^{-4}-6.37\times10^{-7}\tau+7.88\times10^{-9}\tau^2+4.8\times10^{-10}\tau^3)+v^3(1.3\times10^{-6}+2.0\times10^{-8}\tau)].$$

Next we calculate $Q_r(v)e^{0.018{,}192{,}7v^2/\tau}$ as a power series in $v$; the result is

$$p(v)=378.774\tau[0.999{,}999+0.000{,}880/\tau+\cdots+v^8(4.55\times10^{-9}/\tau^4)],$$

which may be represented as

$$p(v)=378.774\tau\sum_{n=0}^{8}g_nv^n.$$

Finally

$$Q=\sum_{v=0}^{\infty}p(v)e^{-3.08660v/\tau},$$

which may be written

$$Q=378.774\tau(1-z)^{-1}\sum_{n=0}^{8}f_ng_n,$$

where

$$z=e^{-3.086{,}60/\tau}$$

and

$$f_n=(1-z)\sum_{v=0}^{\infty}v^nz^v.$$

TABLE II. *Thermodynamic functions for carbon monoxide.**

| $T$, °K | $-(F_0-E_0^0)/T$ | $H$ | $S$ | $C_P$ | $T$, °K | $-(F_0-E_0^0)/T$ | $H$ | $S$ | $C_P$ |
|---|---|---|---|---|---|---|---|---|---|
| 50 | 27.975 | 345.94 | 34.894 | 6.954 | 1500 | 51.867 | 11342 | 59.428 | 8.395 |
| 100 | 32.777 | 693.61 | 39.713 | 6.953 | 1625 | 52.475 | 12397 | 60.103 | 8.469 |
| 200 | 37.588 | 1388.9 | 44.533 | 6.952 | 1750 | 53.042 | 13459 | 60.733 | 8.532 |
| 300 | 40.405 | 2084.3 | 47.352 | 6.959 | 1875 | 53.575 | 14529 | 61.324 | 8.586 |
| 400 | 42.404 | 2782.2 | 49.360 | 7.007 | 2000 | 54.077 | 15605 | 61.879 | 8.631 |
| 500 | 43.958 | 3487.8 | 50.934 | 7.115 | 2250 | 55.001 | 17773 | 62.900 | 8.706 |
| 600 | 45.233 | 4206.7 | 52.244 | 7.269 | 2500 | 55.838 | 19957 | 63.821 | 8.763 |
| 700 | 46.317 | 4942.3 | 53.378 | 7.443 | 2750 | 56.602 | 22153 | 64.658 | 8.808 |
| 800 | 47.264 | 5695.3 | 54.383 | 7.616 | 3000 | 57.306 | 24360 | 65.426 | 8.845 |
| 900 | 48.106 | 6465.0 | 55.289 | 7.776 | 3250 | 57.958 | 26575 | 66.135 | 8.876 |
| 1000 | 48.866 | 7249.8 | 56.116 | 7.918 | 3500 | 58.566 | 28798 | 66.794 | 8.903 |
| 1100 | 49.560 | 8048.1 | 56.877 | 8.043 | 4000 | 59.671 | 33261 | 67.986 | 8.946 |
| 1200 | 50.200 | 8857.9 | 57.581 | 8.151 | 4500 | 60.654 | 37742 | 69.042 | 8.982 |
| 1300 | 50.793 | 9677.8 | 58.237 | 8.245 | 5000 | 61.542 | 42241 | 69.990 | 9.012 |
| 1400 | 51.347 | 10506. | 58.851 | 8.325 | | | | | |

* Nineteen of the temperatures in this table are also used by Clayton and Giauque; comparison of the values of $-(F_0-F_0^0)/T$ in the two tables shows exact agreement 14 times; the values of the present table are 0.001 lower four times, and 0.001 higher once.

The sums $f_n$ have been given previously.[13] The factor $\Sigma f_n g_n$ represents the effect of all the anharmonic, stretching and coupling terms. In the present case we can calculate all of the thermodynamic functions separately for this factor and add them to the values for a rigid rotator and harmonic oscillator given by the other factor. Accordingly, we calculate also $f_n'$, $f_n''$, $g_n'$, $g_n''$, where a $'$ means differentiation with respect to $1/T$. Since the $g_n$ are power series in $T$ and $1/T$, their derivatives may be written down without calculation. The $f_n$ are the same in all problems and their derivatives may thus be tabulated; the interested reader can easily prepare such a table for his own use.

The calculation has been carried out at 300, 500, 750, 1000, 2000, 3000, 4000 and 5000°K. Over this entire range the anharmonic correction is represented by

$$F/T=-0.548-0.30/T+0.009{,}66\ln T+1.193{,}45\times10^{-5}T^2-1.5625\times10^{-10}T^3.$$

This equation and its derivatives reproduce the calculated values for $F/T$, $H/T$ and $C_P$ in every case to 0.001 cal./deg. or better. It may thus be used with complete confidence to calculate the values at any intermediate temperature. The final values at a few temperatures are given in Table II.

[13] Kassel, Phys. Rev. **43**, 364 (1933).

# The Quantum Mechanics of Chemical Reactions Involving Conjugate Double Bonds[1]

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The various theories of conjugate double bonds are discussed on the basis of quantum mechanics. The potential energy surfaces for the addition of diatomic molecules to such bonds are calculated by the generalized Heitler-London method. It is shown that various mechanisms are possible for such reactions and that such effects as the steric repulsions of the various inactive groups in the molecule and the nature of the catalytic surface on which such reactions often take place determine whether 1–2 or 1–4 addition takes place.

THE term "conjugate double bonds" is applied by organic chemists to those compounds which contain two double bonds joining pairs of atoms which are joined to each other by a single valence bond. For example in butadiene

$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$$

the double bonds joining carbon atoms 1–2 and 3–4 are "conjugate," and in acrolein

$$H_2C=CH-CH=O$$

the C = C double bond and the C = O double bond are conjugate.[2]

Under certain conditions such systems of double bonds exhibit abnormal behavior. For example, when molecules containing the group

$$\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}$$

are hydrogenated it is frequently found that the hydrogen is added, not to atoms 1 and 2 or 3 and 4, but to atoms 1 and 4, a new double bond being formed between atoms 2 and 3:

$$\overset{1}{CH}-\overset{2}{C}=\overset{3}{C}-\overset{4}{CH}.$$

To account for this and similar phenomena, Thiele[3] introduced a theory of "partial valencies." According to Thiele atoms joined by double bonds exhibit a residual or partial valence which he indicated by dotted lines

$$C=C \qquad C=O \qquad C=N.$$

The addition of molecules such as $H_2$ to such double bonded atoms may then be represented by the following steps:

$$C=C+H_2\rightarrow C=C\rightarrow \underset{H}{C}-\underset{H}{C}$$

the hydrogen first being attached by the partial valences, which then rearrange to normal bonds.

In a system of conjugate double bonds the partial valences of the adjoining atoms 2 and 3 would satisfy each other, so that such a system might be represented by

$$\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}$$

the curved line representing the union of two partial valences. Since atoms 2 and 3 now have no residual valence, addition of molecules such as $H_2$ might now be expected to take place on atoms 1 and 4, the partial valence bond between atoms 2 and 3 becoming an ordinary double bond.

Another view of this type of reaction has been proposed by Erlenmeyer[4] who regarded the re-

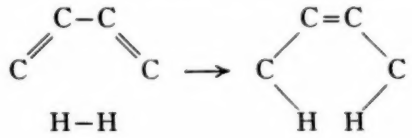
[1] Preliminary reports of this work have been published in *Science News Letter* **23**, 5 (1933), and Science **77**, 158 (1933).

[2] For a fuller discussion of conjugate double bonds see Cohen, *Organic Chemistry*, 5th ed. (Longmans, Green, N. Y.) Vol. 1, pp. 144–163.

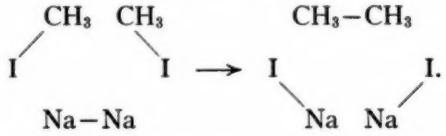
[3] Thiele, Ann. d. Chemie **306**, 87 (1899).

[4] Erlenmeyer, Ann. d. Chemie **316**, 43 (1901).

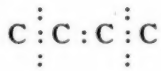
action as a simple rearrangement of bonds



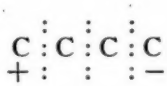
analogous to such reactions as



Other theories have been suggested by Lapworth[5] and by Kermack and Robinson[6] which are based on the Lewis-Langmuir theory of valence. If we represent the conjugate system by the electronic formula



these authors assume that an electron shift occurs to the form



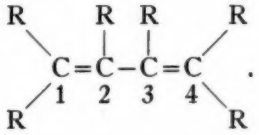
in which one end carbon atom has gained an electron and the other lost an electron, the remaining electrons forming a series of three-electron bonds. The polarity of the end carbon atoms then attracts the molecule which is about to be added.

A quantum mechanical interpretation of the Lapworth-Kermack-Robinson mechanism is difficult. While it is quite possible that the three-electron bonds postulated by them do exist,[7] in the particular case of conjugate double bonds such states almost certainly have a high energy, and cannot therefore be present in any large amount at ordinary temperatures. Moreover, in the case of symmetrical molecules such as butadiene, the polarity would oscillate from one end to the other with a very high frequency, so that the mean charge on any atom would be zero during the comparatively slow approach of an additive molecule. This theory cannot therefore be considered satisfactory.

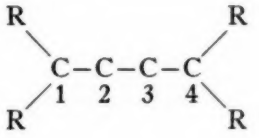
The Thiele theory is not without a quantum mechanical basis. If we consider only the four electrons entering into the two double bonds, it is possible to set up an eigenfunction corresponding to bonds between atoms 1–2 and 3–4 and another eigenfunction corresponding to bonds 1–4 and 2–3. The actual normal state of the molecule has for its eigenfunction a linear combination of these two ways of drawing the valence bonds. Since, however, the interaction energy of two carbon atoms as far apart as atoms 1 and 4 is quite small, the energy of the second system of bonds must necessarily lie much higher than that of the first system and consequently it is to be expected that the normal state of the molecule contains very little of the second way of drawing the bonds. But Thiele's picture of the conjugated system is essentially the second way of drawing the bonds, for the bond between atoms 1 and 4 is so weak that the electrons are practically free. Since we have seen that this way of drawing the bonds is unimportant in the normal state, we must discard Thiele's picture.

Erlenmeyer's hypothesis, on the other hand, seems to be free from any qualitative objections, but an estimate of the activation energy of some typical examples of 1–4 addition reactions is necessary before its validity can be established.

Suppose therefore that we consider the addition of a molecule AB, composed of two univalent atoms, to the conjugate double bonds of some substituted butadiene:



We may regard this molecule as a fixed system



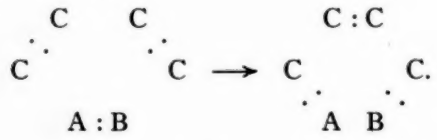
plus four electrons, one on each carbon atom, which normally form the second bond between atoms 1–2 and 3–4. In the Lewis-Langmuir

[5] Lapworth, Trans. Chem. Soc. **121**, 416 (1922).

[6] Kermack and Robinson, Trans. Chem. Soc. **1212**, 427 (1922).

[7] See, for example, Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

notation we may then write the essential part of the reaction as




The quantum mechanical calculation of the energy of activation of a reaction in which six electrons take part has been described by Sherman and Eyring.[8] We have carried out this calculation for the case in which A and B are bromine atoms or hydrogen atoms. The constants used to determine the necessary Morse potential energy curves are given in Table I. $D$ is the heat

TABLE I.

| Molecule | $D$ | $D'$ | $\omega_0$ | $r_0$ | $a$ |
|---|---|---|---|---|---|
| C–C | 74.5 | 75.6 | 1620 | 1.46 | 2.11 |
| C–Br | 65.3 | 66.1 | 557 | 2.05 | 1.45 |
| C–H | 92 | 96.2 | 2920 | 1.13 | 1.88 |
| H–H | 102.4 | 108.6 | 4375 | 0.74 | 1.942 |
| Br–Br | 45.2 | 45.7 | 323.9 | 2.28 | 1.98 |

of dissociation in kg cal., $D'$ the heat of dissociation plus the half quantum of vibrational energy, $\omega_0$ the vibrational frequency in $cm^{-1}$, $r_0$ the normal separation of the atoms in A and $a$ is Morse's constant. In every case it was assumed that the coulombic integral was 14 percent of the total energy.

Assuming that the valences of any carbon atom are directed toward the vertices of a regular tetrahedron, and that when two carbon atoms are joined by a double bond these tetrahedra are placed so that they have an edge in common, the four carbon atoms in the butadiene structure lie in a broken line, the angles at atoms 2 and 3 being arc cos $(-1/\sqrt{3})$ $=125°\ 16'$. In the normal state of the molecule there will be free rotation about the single bond joining atoms 2 and 3. The most favorable orientation for 1–4 addition is that in which the four carbon atoms lie in a plane, with atoms 1 and 4 on the same side of the line joining atoms 2 and 3. The atoms A and B of the molecule AB

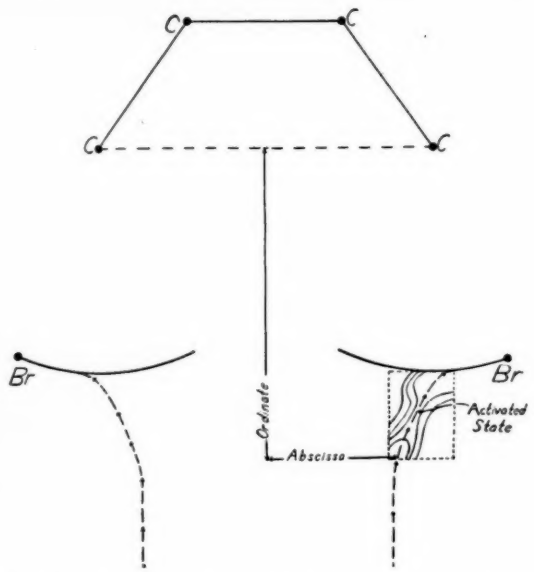
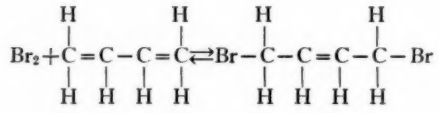



FIG. 1. Addition bromine to the 1–4 carbon atoms in butadiene.




can then most easily approach in the same plane. The situation is shown in Fig. 1 for the case of $Br_2$ addition.

If the molecule AB remains symmetrically placed with respect to the carbon atoms the configuration can be completely specified by two coordinates: $x$, the distance of the center of the molecule AB from the line joining the two atoms on which addition is to take place, and $y$, the distance between the atoms A and B. During the course of the reaction the molecule AB will at first approach the butadiene molecule, that is, $x$ will decrease, while $y$ will remain almost constant. Finally, however, $y$ will begin to increase and the molecule will divide into two atoms attached to carbon atoms 1 and 4.

We have calculated the energy of this system in the two cases when AB is $Br_2$ and $H_2$ for a sufficient number of values of $x$ and $y$ to be able to construct a contour map of the energy as a function of $x$ and $y$. The energy surface shows a valley coming in from $x=+\infty$, whose bottom, for large $x$, follows the line $y=r_0$, the normal distance of the molecule AB. Near the carbon

[8] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932). See also Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 70 (1933).

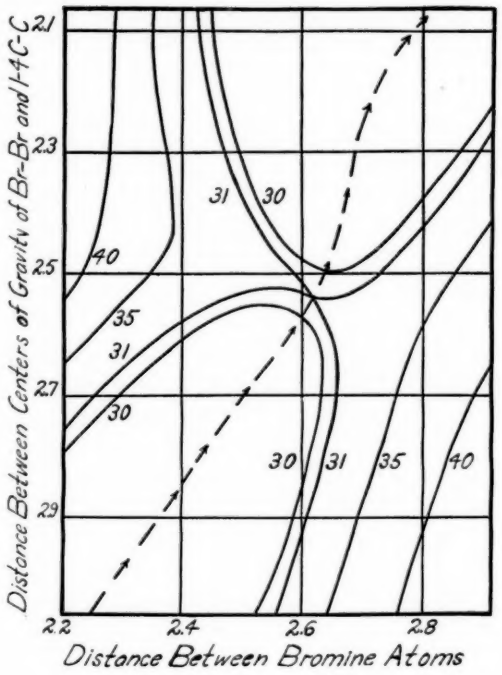



FIG. 2. Potential energy surface for the reaction

atoms the valley turns outward and finally runs into a sort of circular trough at the normal distance for the C–A molecule. The path of the valley floor is shown as a dotted line in Fig. 1. As the path turns the valley floor rises, reaches a maximum height and drops again. An enlargement of the portion of the energy surface near the top of the pass is shown in Fig. 2. It can be seen from this figure that an energy of 31.3 kg calories is required to surmont the potential barrier. A similar surface for the 1–4 addition of $H_2$ shows an activation energy of 64.0 kg calories.

If the additive molecule does not approach in the same plane as the four carbon atoms, the activation energy is found to be higher. For example, if bromine approaches along a line perpendicular to this plane the activation energy rises to 65.0 kg calories, and if the approach is along a line making an angle of 109° to the plane, the activation energy is 40.3 kg calories. The positions of the activated points and the activation energies for molecules approaching along different paths are shown in Table II. This table gives the activation energies of the molecules AB shown in the first column adding to the carbon atoms shown in the second column when the line of approach makes the angle given in the third column with the plane of the carbon atoms. The next two columns give the $x$ and $y$ coordinates of the system at the activated point. $Q_{act.}$ is the coulombic binding at this point, $I_{act.}$ the interchange binding at this point and $E_{act.}$ the total binding. $E_0$ is the total binding when the molecule AB is at a great distance from the butadiene molecule, so that $E_0 - E_{act.}$ is the activation energy of the reaction. The table also includes the results obtained from the calculation of similar surfaces showing the process of 1–2 addition. Examples of these surfaces are shown in Figs. 3 and 4.

From Table II it may be seen at once that it is much easier for addition to take place in the 1–4 position than in the 1–2 position, and that the easiest direction of approach is in the plane of the carbon atoms. These activation energies, however, take no account of the groups which may be substituted on the butadiene molecule. As has been discussed elsewhere[9] the remaining atoms

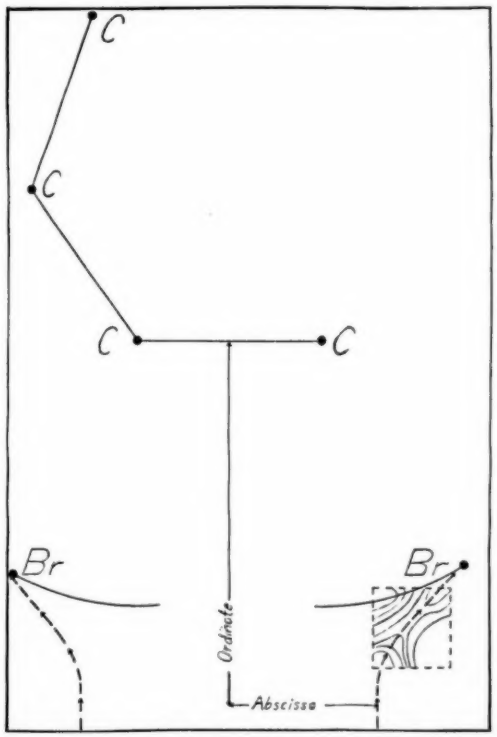



FIG. 3. Addition of bromine to the 1–2 carbon atoms in butadiene.

[9] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

TABLE II.

| AB | Pos. | Angle | $x$ | $y$ | $Q_{act.}$ | $I_{act.}$ | $E_{act.}$ | $E_0$ | $E_0-E_{act.}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Br_2$ | 1–4 | 180° | 2.5 | 2.6 | 64.0 | 78.2 | 142.2 | 173.4 | 31.3 |
| $Br_2$ | 1–4 | 109° | 2.4 | 2.6 | 65.5 | 67.0 | 132.5 | 172.8 | 40.3 |
| $Br_2$ | 1–4 | 90° | 2.3 | 2.6 | 74.2 | 34.2 | 108.4 | 173.4 | 65.0 |
| $H_2$ | 1–4 | 180° | 2.2 | 1.1 | 87.5 | 84.8 | 172.3 | 236.3 | 64.0 |
| $Br_2$ | 1–2 | 90° | 2.2 | 2.6 | 76.7 | 39.7 | 116.4 | 172.6 | 56.2 |
| $Br_2$ | 1–2 | 180° | 2.1 | 2.8 | 69.4 | 62.3 | 131.7 | 173.4 | 41.7 |
| $H_2$ | 1–2 | 180° | 1.3 | 0.88 | 81.9 | 72.8 | 154.7 | 236.3 | 81.6 |

of the molecule exert a force equal to one-half the interchange force which would be exerted if there were bonds joining the atoms to the molecule AB, less the coulombic attraction. Thus the substitution of a methyl group for one of the hydrogen atoms on carbon atom 4 might easily create enough repulsion to make 1–2 addition easier than 1–4 addition. The exact calculation of these repulsive forces is however complicated by the fact that the carbon eigenfunctions are not the spherically symmetric sort postulated in the work just mentioned but instead are concentrated in the tetrahedral directions characteristic of carbon. A simple calculation would therefore greatly overestimate the strength of the repulsions.

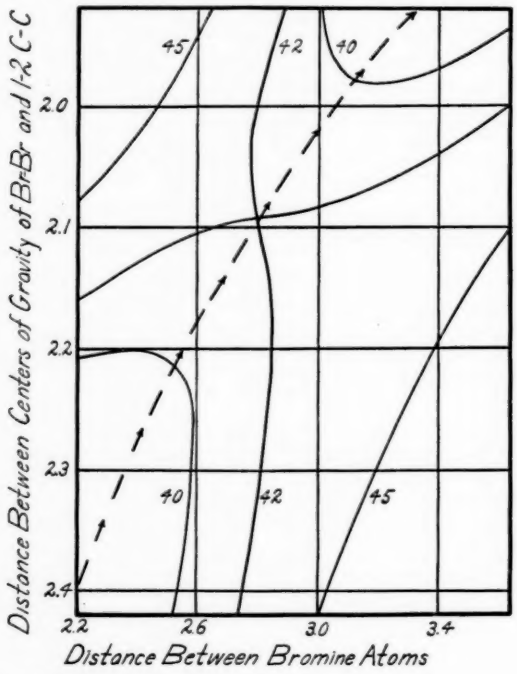
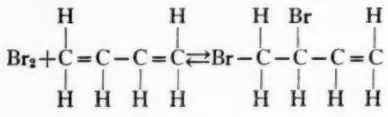



FIG. 4. Potential energy surface for the reaction



Regardless of these repulsions, the activation energies given in Table II are a lower limit, and since these activation energies are all of the order of 30–60 kg calories, these reactions will be extremely slow at room temperatures. Since it is found experimentally that reactions between bromine and conjugated systems are fast reactions in general, we must search for still other possible mechanisms, such as catalysis by a surface.

Heisig[10] has shown that the reaction between gaseous butadiene and bromine takes place largely on the surface of the glass vessel in which the reaction takes place. A detailed consideration of the possible reaction mechanisms on surfaces of various kinds is too complicated to be carried out at present, but certain possibilities may be noted. A very probable mechanism is one similar to that suggested by Sherman and Eyring[11] for the ortho-para hydrogen conversion on catalysts such as activated charcoal.[12] If this mechanism

[10] Heisig, J. Am. Chem. Soc. **55**, 1297 (1933).

[11] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).

[12] Bonhoeffer, Farkas and Rummel, Zeits. f. physik. Chemie **21B**, 225 (1933), object to this mechanism as an explanation for the ortho-para hydrogen conversion at low temperatures but accept it at room temperature and above. It is for these higher temperatures it is of interest here.

can be extended to the case we are now considering we might regard the conjugate linkage joined to the surface of the catalyst by bonds from carbon atoms 1 and 2 or 1 and 4. The additive molecule might be adsorbed on a nearby portion of the surface. When desorption takes place, both molecules may desorb together and simultaneously form a single molecule. Whether this molecule is the 1–2 or 1–4 addition product depends on such factors as the spacing of the active atoms in the surface and the method of attachment of the butadiene molecule. Further consideration of this mechanism would therefore require more data than are available at present.

Another possible mechanism would involve the attachment of the butadiene molecule to the surface by only one bond, probably to carbon atom 1. This gives a free electron on atom 2 which in turn tends to loosen the electrons on atoms 3 and 4. The electrons on atoms 2, 3 and 4 are then in the same state as the electrons on three univalent atoms. Two of the three electrons will always form a bond between atoms 2 and 3 or 3 and 4, while the third electron will be free. The bond, however, will oscillate rapidly between 2–3 and 3–4, so that the electrons on atoms 2 and 4 are each half the time. If now a bromine or other additive molecule strikes the free end of the conjugate system, the carbon atom struck behaves very much like a free monovalent atom, and with a small activation energy may attach itself to one of the bromine atoms, leaving the other bromine atom free. A quantum mechanical calculation of the activation energy of this reaction gives 13 kg calories, indicating that the reaction may go at a very rapid rate at room temperatures. The bromine atom resulting can, with a calculated activation energy also of 13 kg calories, curiously enough, add itself to the 1 carbon atom of another butadiene molecule, forming a molecule in a condition similar to that of a molecule attached to a surface, and having the same two half-free electrons. This molecule can then react with a bromine molecule to form a molecule of the dibrom addition product and a new bromine atom which may carry on the chain. The reaction mechanism may be represented by the following equations:

$$S- +C=C-C=C \rightarrow S-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$$

$$S-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}+Br_2 \rightarrow S-C-C=C-C-Br+Br$$

$$Br- +C=C-C=C \rightarrow Br-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$$

$$Br-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}+Br_2 \rightarrow Br-C-C=C-C-Br+Br$$

where S is a surface atom. It might be argued against this mechanism that in the case of the addition of an unsymmetrical molecule AB to the conjugate linkage a mixture of the A–A and B–B addition products should be formed with the A–B addition product. This is not observed. This would, however, not necessarily be true, for in general the activation energies for the reactions

$$X-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}+AB \rightarrow X-C-C=C-C-A+B$$

$$X-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}+AB \rightarrow X-C-C=C-C-B+A$$

will be sufficiently different that one of them will occur much more readily than the other. Suppose that the first of these reactions predominates. Then the chain will be carried on by the B atoms alone so that the X in $X-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$ will always be B, and only the AB addition product will be formed.

A more serious difficulty with this reaction scheme arises from the fact that the bond $S-(C-C=C-C-Br)$ is much stronger than the bond $S-(\overset{|}{C}-\overset{|}{C}-\overset{|}{C})$, so that the rate of desorption of $-C-C=C-C-Br$ radicals will be slow. The surface will therefore soon become

poisoned and the reaction will stop. For this reason we believe the first surface mechanism to be the more likely in the majority of cases. The second mechanism, however, is probably the course of photochemical addition reactions, the atoms formed by the photochemical dissociation of the additive molecule initiating chains of this type. The rôle played so often by oxygen in polymerizations may well be due to a similar effect, the reaction mechanism being of the type

$$O_2+C=C-C=C\rightarrow O_2-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$$

$$O_2-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}+C=C-C=C$$

$$\rightarrow O_2-C-C=C-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$$

and so on, each successive addition activating the end of the last molecule added to the chain.

Similar reaction chains may sometimes arise from the thermal decomposition of the molecule AB into atoms assuming again that the B atoms carry on the chain. The reaction initiated in this way will have a rate governed by an expression of the type

$$d[\mathrm{BuAB}]/dt = kK^{\frac{1}{2}}[\mathrm{AB}]^{\frac{1}{2}}[\mathrm{Bu}],$$

where [Bu] is the concentration of the butadiene molecule, [BuAB] is the concentration of the addition product, and [AB] is the concentration of AB. $k$ is the rate constant for the reaction

$$B+C=C-C=C\rightarrow B-C-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}$$

and $K$ is the equilibrium constant [A][B]/[AB]. Now $K$ varies with temperature essentially according to the law $e^{-X/RT}$ where $X$ is the heat of dissociation of AB. $k$ varies as $e^{-E/RT}$ where $E$ is the activation energy of this reaction. Substituting these quantities in the expression for the total rate we find a factor $e^{-(E+X/2)/RT}$ for the temperature dependence of the rate. In other words the effective activation energy for the whole mechanism is $E+X/2$. If this is lower than the activation energy for the direct addition reaction this mechanism will be preferred. We have seen that for $Br_2$, $E$ is 13 kg calories and $X$ is 46 kg calories, so that $X/2+E$ is 36 kg calories, which is slightly higher than the activation energy of the direct addition process. The difference here is so small that under suitable conditions both reactions may be operative.

From these considerations it becomes clear that the theory of reactions involving conjugate linkages cannot be explained in terms of the structure of the conjugate system alone, for during the course of the reaction this structure may be greatly modified by the other reactant. Further study of the kinetics of these addition reactions may reveal examples of all of the mechanisms we have discussed. There seems to be no general rule for predicting the course of such reactions but the construction of the proper set of energy surfaces in each individual case.

# The Normal State of the Hydrogen Molecule

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(Received May 8, 1933)

A simple wave function for the normal state of the hydrogen molecule, in which both the atomic and ionic configurations are taken into account, was set up and treated by a variational method. The dissociation energy was found to be 4.00 v.e. as compared to the experimental value of 4.68 v.e. and Rosen's value of 4.02 v.e. obtained by use of a function involving complicated integrals. It was found that the atomic function occurs with a coefficient 3.9 times that of the ionic function. A similar function with different screening constants for the atomic and ionic parts was also tried. It was found that the best results are obtained when these screening constants are equal. The addition of Rosen's term to the atomic-ionic function resulted in a value of 4.10 v.e. for the dissociation energy.

ATTEMPTS to obtain some of the properties of the normal hydrogen molecule by wave-mechanical methods date to the early days of wave mechanics. Heitler and London[1] applied a first-order perturbation method, and Sugiura,[2] by evaluating an integral whose value Heitler and London had only estimated, obtained results qualitatively comparable with known experimental data. Eisenschitz and London[3] applied a second-order perturbation treatment and obtained results in poorer agreement with experimental values than the results of previous calculations. For example, Heitler-London-Sugiura's value for the dissociation energy is 3.2 v.e. and the experimental value corrected for the zero point energy is 4.68 v.e., while Eisenschitz and London obtained 9.5 v.e. Thus it seems that the perturbation method is not very satisfactory for the treatment of the hydrogen molecule. The variational method, by approaching the value of energy from one side, is safe from the possibility of overshooting the mark. Wang,[4] using a variational method involving the introduction of a shielding constant as a parameter, obtained 3.7 v.e. for the dissociation energy. Rosen,[5] by using the three-parameter function $\psi=\psi^0+\sigma\psi'$, where $\psi^0$ is the hydrogenic wave function for the lowest state with a shielding constant $Z$, $\psi'$ is a function symmetrical about the axis but not about a plane through the nucleus perpendicular to it, and $\sigma$ is a parameter, has obtained 4.02 v.e. for the dissociation energy. The improvement on the previous value is considerable, but the calculations are rather laborious.

All these calculations were based on the assumption that each of the nuclei always has one electron attached to it, these electrons sometimes interchanging their positions, which leads to the interchange energy. It was suggested by Hund and Mulliken[6] that a truer picture would be given by a wave function $(\psi_1+\varphi_1)(\psi_2+\varphi_2)$ which takes account not only of the atomic configuration but also of the ionic configuration, when both electrons are on the same nucleus, the other being completely stripped of electrons. However, a function of the type suggested by Hund and Mulliken would give the hydrogen molecule in the normal state as much ionic character as atomic. There seems to be no reason to assume this, and a logical wave function to take care of the atomic-ionic character of the hydrogen molecule appears to be

$$c(\psi_1\varphi_2+\varphi_1\psi_2)+(\psi_1\psi_2+\varphi_1\varphi_2)$$

where $c$ is a parameter,

$$\psi_1=Ne^{-Zr_{A1}} \quad \text{and} \quad \varphi_1=Ne^{-Zr_{B1}}.$$

* Contribution No. 364.

[1] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[2] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[3] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1927).

[4] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[5] N. Rosen, Phys. Rev. **38**, 2099 (1931).

[6] F. Hund, Zeits. f. Physik **73**, 1 (1931).

It has been shown[7] that the integral

$$E=\int \varphi^* H\varphi d\tau / \int \varphi^* \varphi d\tau,$$

where $H$ is the Hamiltonian operator and $\varphi$ is a function which satisfies certain boundary conditions but is otherwise arbitrary, containing, say, some variable parameters, has the property that the lowest value $W$ obtained from varying the numerical parameters is the best approximation to the value of $E$, and that $E-W$ is always positive or zero. Hence the variational integral presents, as already mentioned, a satisfactory means for evaluating the energy of the normal state of the hydrogen molecule.

The first test for the wave function

$$\psi=c(\psi_1\varphi_2+\varphi_1\psi_2)+(\psi_1\psi_2+\varphi_1\varphi_2)$$

would be to consider it a two-parameter function. The results obtained by varying $c$ would then be comparable with the Heitler-London-Sugiura results. It is, however, more convenient to treat

$$\psi=c(\psi_1\varphi_2+\varphi_1\psi_2)+(\psi_1\psi_2+\varphi_1\varphi_2)$$

as a three-parameter function, and then, at a certain point in the algebra, to reduce it to a two-parameter function by letting $Z=1$.

It is useful to set up the following scheme, devised by Slater:

| | I | II | III | IV |
|---|---|---|---|---|
| $\psi$ | + | − | +− | |
| $\varphi$ | − | + | | +− |

and rewrite our wave function as

$$\psi=c(\psi_{\rm I}-\psi_{\rm II})+\psi_{\rm III}+\psi_{\rm IV}, \tag{1}$$

where $\psi_{\rm I}-\psi_{\rm II}$ is the atomic Heitler-London term and $\psi_{\rm III}+\psi_{\rm IV}$ is the ionic term. The variational integral

$$W=\int \psi^* H\psi d\tau / \int \psi^* \psi d\tau \tag{2}$$

then takes the form

$$W=\frac{W_N}{d}=\frac{\int H[c(\psi_{\rm I}-\psi_{\rm II})+\psi_{\rm III}+\psi_{\rm IV}]^2 d\tau}{\int [c(\psi_{\rm I}-\psi_{\rm II})+\psi_{\rm III}+\psi_{\rm IV}]^2 d\tau}. \tag{2a}$$

The wave equation for a hydrogen-like atom, in a system of units where unit of length $a_0=0.52845$A and unit of energy $e^2/a_0=27.06$ volt-electrons, is

$$\nabla^2\psi+2(W-V)\psi=0 \tag{3}$$

or, in a rewritten form,

$$W\psi=-\tfrac{1}{2}\nabla^2\psi+V\psi, \tag{3a}$$

where $W=-Z^2/2$. The general wave equation may be written as

$$W\psi=H\psi, \tag{4}$$

with

$$H=-\tfrac{1}{2}\nabla^2+V \quad \text{and} \quad V=\Sigma\Sigma(Z_iZ_j/r_{ij}), \tag{5}$$

the Hamiltonian function for the case of a hydrogen molecule being

$$H=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2) - \frac{1}{r_{A1}}-\frac{1}{r_{A2}}-\frac{1}{r_{B1}}-\frac{1}{r_{B2}}+\frac{1}{r_{12}}+\frac{1}{r_{AB}}. \tag{6}$$

In subsequent calculations the letter $I$ with a subscript will be used to indicate the different integrals occurring. The integral $\int \psi\varphi d\tau$ will be denoted by $s$.

Leaving out for the present the term $1/r_{AB}$ in the Hamiltonian we can now set up the following expressions:

$$\int \psi_1 H_1 \psi_1 d\tau_1 = \int \psi_1 \left(-\frac{\nabla_1^2}{2}-\frac{1}{r_{A1}}-\frac{1}{r_{B1}}\right)\psi_1 d\tau_1$$

$$= \int \psi_1 \left(-\frac{Z^2}{2}+\frac{Z-1}{r_{A1}}-\frac{1}{r_{B1}}\right)\psi_1 d\tau_1$$

$$= -[Z^2/2+(1-Z)Z+I_1]=A \tag{7}$$

$$\int \psi_1 H_1 \varphi_1 d\tau_1 = -[(Z_2/2)s+(2-Z)I_2]=B. \tag{7a}$$

Let us denote integrals of the type $\int \psi_1 H \psi_{\rm II} d\tau$ by $H_{\rm I\,II}$. These integrals may be represented also by $\Sigma_p(-)^p(\psi\varphi/H/\psi\varphi)$, where $p$ stands for the number of permutations of the signs of the spin that are necessary to obtain the same spin for functions pertaining to the same electron. Then, in terms of $A$ and $B$, we obtain

$$\begin{aligned} &H_{\rm I\,I}=H_{\rm II\,II}=2A+I_4;\ H_{\rm IV\,III}=H_{\rm IV\,IV}=2A+I_3,\\ &H_{\rm I\,II}=H_{\rm II\,I}=-2Bs-I_6;H_{\rm III\,IV}=H_{\rm IV\,III}=2Bs+I_6,\\ &H_{\rm I\,III}=H_{\rm III\,I}=H_{\rm I\,IV}=H_{\rm IV\,I}=-H_{\rm II\,III}=-H_{\rm III\,II}\\ &\quad=-H_{\rm II\,IV}=-H_{\rm IV\,II}=As+B+I_5. \end{aligned} \tag{8}$$

[7] C. Eckart, Phys. Rev. **36**, 878 (1930).

Making use of the relations (8), we find

$$\tfrac{1}{2}W_N = c^2H_{\mathrm{I\,I}} + H_{\mathrm{III\,III}} - c^2H_{\mathrm{I\,II}} + H_{\mathrm{III\,IV}} + 4cH_{\mathrm{I\,III}}$$
$$= c^2(2A+I_4) + 2A + I_3 + c^2(2Bs+I_6) + 2Bs + I_6 + 4c(As+B+I_5) \quad (9)$$

and putting $I = ZF$, where $F$ is a function of $\rho(=Zr_{AB})$ only, this becomes

$$\tfrac{1}{2}W_N = Z^2[(c^2+1)(1+2sF_2-s^2)+4cF_2] + Z[(c^2+1)(F_6-2-2F_1-4sF_2)$$
$$+F_3+c^2F_4-4c(s+F_1s+2F_2-F_5)] = \lambda Z^2+\mu Z, \quad (9a)$$

where

$$\lambda = (c^2+1)(1+2sF_2-s^2)+4cF_2 \quad (10)$$

$$\mu = (c^2+1)(F_6-2-2F_1-4sF_2)+F_3+c^2F_4-4c(s+F_1s+2F_2-F_5). \quad (10a)$$

The denominator in the expression for $W$ has the value

$$d = \int \psi^*\psi d\tau = 2d_{\mathrm{I\,I}} + 2d_{\mathrm{III\,III}} - 2d_{\mathrm{I\,II}} + 2d_{\mathrm{III\,IV}} + 8d_{\mathrm{I\,III}}$$
$$= 2c^2+2+2c^2s^2+2s^2+8cs = 2[(c^2+1)(1+s^2)+4cs] = 2\nu. \quad (11)$$

As $\rho = Zr_{AB}$, introducing the term $1/r_{AB}$ that we left out of the calculations, we have

$$W = (\lambda Z^2+\mu Z)/\nu + Z/\rho = (\lambda/\nu)Z^2 + (\mu/\nu+1/\rho)Z. \quad (12)$$

Substituting $Z=1$ in (12) we obtain $W$ as a function of parameters $c$ and $\rho$:

$$W = \frac{\lambda+\mu}{\nu} + \frac{1}{\rho} = \frac{(c^2+1)(-1-s^2-2F_1-2F_2s+F_6)+F_3+c^2F_4-4c(s+F_1s+F_2-F_5)}{(c^2+1)(1+s^2)+4cs} + \frac{1}{\rho}. \quad (13)$$

Minimizing (13) with respect to $c$, $dW/dc=0$ yields a quadratic in $c$. Substituting the value of $c$ obtained from this quadratic back in (13) and varying $\rho$, the lowest value of $W$ was found to be $W=-1.1187$ with $\rho=1.67$ and $c=6.322$. The Sugiura value for $W$ is $W=-1.1156$, so that the inclusion of the ionic term gives an improvement in the dissociation energy of 0.0031 or 3 percent.

Going back to (12), we can improve the treatment by minimizing (12) with respect to $Z$, which is equivalent to Wang's treatment plus an ionic term. We get

$$dW/dZ = (2\lambda/\nu)Z + \mu/\nu + 1/\rho \quad (14)$$

and

$$Z_{\min} = -(\nu/2\lambda)(\mu/\nu+1/\rho). \quad (15)$$

Substituting (15) into (12) we have

$$W_{Z=\min} = -(\nu/4\lambda)(\mu/\nu+1/\rho)^2. \quad (16)$$

Expression (16) is a function of $c$ and $\rho$, as was the case for (13). But while in the case of (13) $dW/dc=0$ gave a quadratic in $c$, in the case of (16) $dW/dc=0$ gives an equation of the fifth degree in $c$. However, to evaluate $c$ by direct substitution of different values of $c$ for a given $\rho$ involves very little labor. The procedure employed was as follows: the best value of $c$ was first obtained for $\rho=1.67$; then $\rho$ was varied to get the best value for the obtained $c$; then $c$ was varied again, and so on, until the variation in either $c$ or $\rho$ would result in a lower value of $W$. The lowest value of $W$ obtained from (16) is $W=-1.148$, with $\rho=1.69$, $c=3.9$ and $Z=1.193$.

This result compares very favorably with the result of Wang's treatment (improvement of 8 percent in dissociation energy) and is just very slightly lower than Rosen's result, which requires very elaborate calculations. Thus the results of this calculation show that the ratio of the coefficients of the atomic and ionic parts of the wave function is about four and not one as was suggested by Hund and Mulliken.

So far it has been assumed that the effective nuclear charge $Z$ is the same for both the atomic and ionic parts. The next step is to introduce a

new parameter $\epsilon = Z'/Z$, where $Z'$ is the effective nuclear charge in the ionic term. On carrying out the calculations* it was found that the value $\epsilon = 1$ gives the lowest energy. This interesting fact shows that the screening constants for the atomic and ionic contributions to the normal state of the hydrogen molecule are the same.

The ionic term and the Rosen term giving independently an improvement in Wang's result, a function including both these terms was set up. As both the Wang-ionic and the Rosen treatment give the same internuclear distance, it is a good approximation to use $\rho = 1.7$ for the Rosen-ionic treatment. With $\rho = 1.7$, $c$ and $\sigma$ were varied until the combination of $c$ and $\sigma$ giving the lowest value for $W$ was obtained.* The results obtained are $W = -1.1515$, $c = 5.7$, $\sigma = 0.07$ and $Z = 1.190$; $\rho$ has not been varied as such a variation would require very long computations and the expected improvement in the value for $W$ was small.

The comparison of the results of the different calculations can be seen from Fig. 1 and from Table I.

TABLE I.

| | $W$ | $\Delta E$(v.e.) | $J_e$(g-cm$^2$) | $\nu_e$(cm$^{-1}$) |
|---|---|---|---|---|
| Present paper | | | | |
| Wang-ionic | −1.148 | 4.00 | $4.65\times10^{41}$ | 4750 |
| Rosen-ionic | −1.1515 | 4.10 | | |
| Heitler-London-Sugiura | −1.116 | 3.14 | 5.2 | 4800 |
| Wang | −1.138 | 3.76 | 4.59 | 4900 |
| Rosen | −1.1485 | 4.02 | 4.65 | 4260 |
| Observed | −1.173 | 4.68 | 4.537[8] | 4418[8] |

The fundamental frequency $\nu_e$ was calculated by means of a Morse[9] function

$$\Delta E = De^{-2a(\rho_0-\rho_m)} - 2De^{-a(\rho_0-\rho_m)}. \qquad (17)$$

By substituting in (17) three different values of $\rho_0$ with the corresponding values of $\Delta E$ we obtain three simultaneous equations which when solved give $D = 0.1479$ and $a = 1.216$. Then $\nu_e$ was calculated from the formula

$$\nu_e = (a/0.1227)(D/M)^{\frac{1}{2}} \qquad (18)$$

where $a$ is in 1/A, $D$ is in wave numbers and $M = M_1M_2/(M_1+M_2)$ is in terms of oxygen = 16.

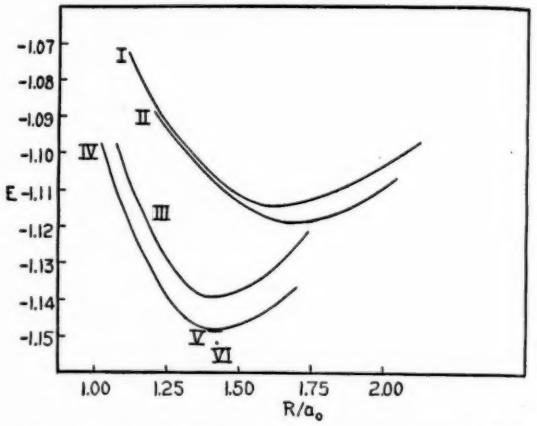


FIG. 1. Calculated energy curves of normal $H_2$. Curve I, Heitler-London; curve II, Heitler-London-ionic; curve III, Wang; curve IV, Wang-ionic; curve V, Rosen; curve VI, Rosen-ionic.

Table I shows that the introduction of the ionic term in the wave function gives an improvement of 8 percent over Wang's value for the dissociation energy of hydrogen molecule. Thus from a simple wave function results almost equivalent to Rosen's were obtained. It should be noticed that while the ionic term corresponds to a definite physical picture, the physical significance of the Rosen term is not very clear. The addition of the Rosen term to the atomic-ionic wave function gives only about $2\frac{1}{2}$ percent increase in the value of the dissociation energy.†

The writer wishes to thank Professor Pauling for suggesting the problem and for valuable criticism during the progress of the work.

* Details of these calculations are in the author's dissertation.

[8] Private communication from Professor Birge.

[9] P. M. Morse, Phys. Rev. **34**, 57 (1929).

† A. S. Coolidge and H. M. James (Phys. Rev. **43**, 588 (1933)) have recently reported a better value for the energy, obtained by the use of a function involving the distance between the two electrons explicitly.

# Statistical Theory of Low Frequency Intermolecular Forces

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The sum of states of a gas consisting of optically anisotropic polar molecules is shown to be substantially equal to the classical Gibbs phase integral at ordinary temperatures. A general method of obtaining the quantum correction to be applied at low temperatures is developed. The intermolecular potential energy appearing in the phase integral is semi-classical in form. The low frequency contribution arising from the permanent dipole moments of the molecules is exactly equal to their mutual electrostatic energy. The high frequency contribution is given by a modification of London's formula in which continuous functions of the molecular orientations occur instead of spatial quantum numbers.

## I.

EXPERIMENTAL evidence seems to support the conclusion that the permanent dipole interaction makes an important contribution to the van der Waals force between polar molecules. For example, the common properties of simple polar substances, such as their higher boiling points and greater tendency for aggregation, give indication of greater cohesive forces than in simple nonpolar substances. Further, a study of the equation of state shows that the virial coefficients of polar gases are much more sensitive to temperature variation than those of nonpolar gases.

In the older theories of van der Waals forces,[1] the rôle of permanent dipoles was comparatively easy to treat. However, in the quantum mechanical theory,[2] several difficulties are encountered. Thus an unambiguous application of perturbation theory is complicated by unsharp degeneracy, arising from the close spacing of the rotational energy levels of the molecules. Further, it seems questionable to treat the approach of the molecules as adiabatic. From the observed specific heats of polyatomic molecules at ordinary temperatures, it is known that there is equipartition of energy between the rotational and translational degrees of freedom. This fact suggests the occurrence of many inelastic collisions involving the interchange of energy between the rotational and translational motion of the molecules. It is likely that the low frequency quantization of two interacting polar molecules is very complicated and does not bear any simple relation to the rotational and translational quantization of two independent molecules.

In the present article no attempt is made to analyze the intermolecular energy states in detail. Instead, the sum of states is calculated directly with the aid of the principle of spectroscopic stability, which permits a calculation of the diagonal sum of a matrix without reference to the actual mode of quantization. If one is interested only in the equilibrium properties of the system, the sum of states furnishes all the information that is required. The general approach to the present problem has many points in common with Van Vleck's treatment of the electric susceptibility of polar molecules. The method developed here may be applied equally well to the latter problem.[3]

Margenau[4] has already shown that the second virial coefficient of a gas consisting of rigid polar molecules without axial spin is closely approximated by the classical expression. The correctness of his conclusion depends upon implicit use of the invariance of the diagonal sum and not upon the type of rotational quanti-

* Contribution from the Research Laboratory of Physical Chemistry, No. 309.

[1] P. Debye, Phys. Zeits. **22**, 178 (1921); W. H. Keesom, Phys. Zeits. **22**, 129, 643 (1921); H. Falkenhagen, Phys. Zeits. **23**, 87 (1922).

[2] F. London, Zeits. f. Physik **63**, 245 (1930).

[3] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Cambridge University Press (1932).

[4] H. Margenau, Zeits. f. Physik **64**, 584 (1930).

zation which he assumes. The present method seems to have certain advantages over that of Margenau. The calculations are made simpler by the use of integrals in momentum space instead of discrete sums over rotational quantum numbers. Further, a general method of obtaining the quantum correction to be applied to the classical result is provided. It is found that Margenau's estimate of the first quantum correction was about fifty percent too high.

## II.

In a recent article, using methods developed by v. Neumann, Wigner and Bloch,[5] we have shown how the sum of states of a gas, consisting of point masses surrounded by conservative fields of force, could be transformed into a phase integral and finally evaluated by expansion in powers of Planck's constant. In the present article, we wish to fix our attention on the relation of the intermolecular force field to the structure and internal motion of the molecules. Therefore, for simplicity, we confine ourselves to a calculation of the sum of states of a single pair of molecules. The sum of states of the entire gas may be constructed to a sufficient degree of approximation for the calculation of the second virial coefficient from those of individual pairs. Further, we neglect corrections introduced by the Bose-Einstein or the Fermi-Dirac statistics, included in the previous article. These have been shown by Uhlenbeck and Gropper[6] to be extremely small even at quite low temperatures.

We take for consideration a pair of molecules confined in a vessel of volume $v$ at the temperature $T$. The first step in the construction of the sum of states of the pair consists in an analysis of the motion to determine the allowed energy states. For the present purposes, it is convenient to speak of two types of motion, the high frequency type and the low frequency type. For the high frequency type, it is assumed that the energy differences $E_n'-E_n$ between excited states $n'$ and the ground state $n$ are very large relative to $kT$, while for the low frequency type it is supposed that the energy difference $E_j'-E_j$ between any two neighboring states $j'$ and $j$ is small relative to $kT$. Further in order that the methods of perturbation theory may be used, it is assumed that the intermolecular perturbation energy is small relative to the high frequency term differences $E_n'-E_n$. This restriction is unnecessary in the case of the low frequency term differences $E_j'-E_j$. At ordinary temperatures the internal motion of the electrons and the vibrational motion of the nuclei in the individual molecules are of the high frequency type. The rotational and translational motion of the molecules belong, on the other hand, to the low frequency type.[7]

The positions of the electrons and nuclei in each molecule of the pair under consideration may be referred to a coordinate system fixed in that molecule with origin at the mean position of its center of gravity. The ensemble of these coordinates will be denoted by $x$, and the Hamiltonian operator associated with the unperturbed electronic and nuclear motion in both molecules by $H(x)$. Additional coordinates are required to specify the orientations of the molecular coordinate systems, the relative position of the centers of gravity of the two molecules and that of their common center of gravity with respect to a reference system fixed in space. Since the motion of the common center of gravity of the pair cannot be influenced by the intermolecular forces, we ignore it in the present calculations. The coordinates specifying the orientations and the relative position of the centers of gravity of the molecules may be denoted by $q$, and the kinetic energy operator associated with their free rotation and translation by $H^0(q)$. The intermolecular potential energy will be a function both of the coordinates

[5] J. v. Neumann, Gött. Nachr. p. 273 (1927); F. Bloch, Zeits. f. Physik **74**, 295 (1932); E. Wigner, Phys. Rev. **40**, 749 (1932); J. G. Kirkwood, Phys. Rev. **44**, 31 (1933).

[6] Uhlenbeck and Gropper, Phys. Rev. **41**, 79 (1932).

[7] We treat here only chemically saturated molecules, the ground states of which are singlet $\Sigma$-states. If spin multiplets are allowed, the problem is complicated by a splitting of the intermolecular energy levels. In the case of soft molecules, the energy spacing of vibrational states may not be large relative to $kT$. However, since the dispersion $f$ values associated with vibrational frequencies are usually small, one may assume that their contribution to the van der Waals force is negligible. Thus temperature excitation of vibrational states, while it would influence the internal specific heat, can reasonably be expected to have little influence on the intermolecular energy.

$x$ and the coordinates $q$ and may be represented by $V(x, q)$. An approximate solution of the dynamical problem may be obtained by treating the low frequency rotation and translation of the molecules in much the same way that the nuclear motion in a polyatomic molecule is treated. One assumes the coordinates $q$ to be fixed and solves the following Schrödinger equation

$$[H(x)+V(x, q)-E]\psi=0. \tag{1}$$

Suppose that the wave functions and energy levels for the unperturbed internal motion are $\psi_n{}^0$ and $E_n{}^0$, where $n$ symbolizes the electronic and vibrational quantum numbers of both molecules. The application of perturbation theory then gives:

$$E_n(q)=E_n{}^0+V_n(q),$$

$$V_n(q)=V_{nn}-\sum{}'_{n'}\frac{|V_{n'n}|^2}{E_{n'}{}^0-E_n{}^0}+\cdots, \tag{2}$$

$$V_{n'n}=\int\psi_{n'}{}^{0*}V(x, q)\psi_n{}^0dx.$$

For every value of the high frequency quantum number $n$, sub-energy levels and wave functions associated with molecular rotation and translation are determined by the equation:

$$\{H^0(q)+V_n(q)-E_{nj}\}\Phi_j=0, \tag{3}$$

where $j$ symbolizes all rotational and translational quantum numbers. The totai energy of the system is then $E_n{}^0+E_{nj}$ and the sum of states may be written:

$$\sigma=\sum_{n',\,j}e^{-\beta(E_{n'}{}^0+E_{n'j})}, \tag{4}$$

where $\beta$ is equal to $1/kT$.

However, if, as we have postulated, the energy difference $E_{n'}{}^0-E_n{}^0$ between an excited state $n'$ and the ground state $n$ is always large relative to $kT$, the contribution of excited electronic and vibrational states to $\sigma$ will be negligible compared with that of the ground state. Thus the sum of states will be very closely approximated by

$$\sigma=e^{-\beta E_n{}^0}\sum_j e^{-\beta E_{nj}}. \tag{5}$$

Since the factor $e^{-\beta E_n{}^0}$ can contribute only pure heat terms to the free energy function, it does not influence the equation of state and we need concern ourselves only with the factor

$$\sigma_n=\sum_j e^{-\beta E_{nj}}. \tag{6}$$

## III.

Let us suppose that the motion of a dynamical system of $M$ degrees of freedom is described in terms of $2M$ canonically conjugate momentum coordinates $p$ and configuration coordinates $q$. We may assume that the wave functions $\Phi_j(q)$ form a complete normal orthogonal set in a restricted portion $\Omega$ of the entire configuration space $\Omega_0$, generated by allowing all of the $q$'s to range from $-\infty$ to $+\infty$. Outside of $\Omega$, we define $\Phi_j$ to be zero. It has been shown[5] that the sum of states is identical with the diagonal sum of the matrix $[e^{-\beta H}]$ where $H$ is the Hamiltonian operator.

$$\sigma=\sum_j[e^{-\beta H}]_{jj}=\sum_j\int_{-\infty}^{+\infty}\Delta_0(q)\Phi_j{}^*(q)e^{-\beta H}\Phi_j(q)dq, \tag{7}$$

$$dq=\prod_{k=1}^{M}dqk.$$

Here $\Delta_0(q)$ is the transformation determinant of the $q$'s. Because of the invariance of the diagonal sum, not only the characteristic functions $\Phi_j$ of the operator $H$, but any other convenient set of orthogonal functions may be used to evaluate $\sigma$. For this purpose we choose the following orthogonal set with continuous characteristic values $p$.

$$U_p(q)=\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h},\qquad \mathbf{p}=\sum_{k=1}^{M}p_k\mathbf{s}_k;\qquad \mathbf{p}\cdot\mathbf{q}=\sum_{k=1}^{M}p_kq_k;\qquad \mathbf{q}=\sum_{k=1}^{M}q_k\mathbf{s}_k, \tag{8}$$

where the $\mathbf{s}_k$ are $M$ mutually orthogonal unit vectors. In the region $\Omega$, $U_p(q)$ may be expanded in terms of the functions $\Phi_j$

$$\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}=\sum_j F_j(p)\Phi_j(q), \quad (a) \qquad F_j(p)=\int_{-\infty}^{+\infty}\Delta_0(q')^{\frac{1}{2}}\Phi_j^*(q')e^{i\mathbf{p}\cdot\mathbf{q}'/h}dq'. \quad (b) \tag{9}$$

The Fourier integral (9b) may be inverted to give

$$\Phi_j(q)=(2\pi h)^{-M}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Delta_0(q')^{\frac{1}{2}}\Phi_j(q')\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot(\mathbf{q}-\mathbf{q}')}dq'dp, \qquad dp=\prod_{k=1}^{M}dpk. \tag{10}$$

When relation (10) is substituted in the integral (7), one obtains

$$\sigma=(2\pi h)^{-M}\int_{-\infty}^{+\infty}\int\int[\textstyle\sum_j\Phi_j^*(q)\Phi_j(q')]\Delta_0(q)\Delta_0(q')^{\frac{1}{2}}e^{-ipq'}e^{-\beta H}\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}dpdq'dq. \tag{11}$$

The summation over the quantum numbers $j$ may be carried out by means of the completeness relation

$$\begin{aligned}\textstyle\sum_j\Delta_0(q)\Phi_j^*(q)\Phi_j(q')&=\prod_{k=1}^{M}\delta(q_k-q_k') \qquad \text{when } q \text{ lies in } \Omega\\ &=0 \quad \text{otherwise}\\ \delta(q-q')&=\delta(q'-q)\end{aligned} \tag{12}$$

where $\delta(q'-q)$ is the Dirac delta-function. When Eq. (12) is introduced into the integral (11) and the integration over $q'$ is carried out, there results

$$\sigma=(2\pi h)^{-M}\int_{-\infty}^{+\infty}\int_{\Omega}\{\Delta_0(q)^{\frac{1}{2}}e^{-i\mathbf{p}\cdot\mathbf{q}/h}e^{-\beta H}\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}\}dpdq. \tag{13}$$

The procedure which has been followed in obtaining Eq. (13) is a generalization of the usual treatment of Fourier integral transformations in a finite one dimensional interval.[8] Because of singularities in the derivatives and possible vanishing of the transformation determinant on the boundary of the region $\Omega$, convergence questions may arise. However, in the present problem, they do not appear to give difficulty.

Before Eq. (13) may be used to evaluate the sum of states, $\sigma_n$, of the pair of molecules considered in the previous section, a more complete specification of the low frequency coordinates $q$ is required. For simplicity the molecules are assumed to be symmetrical rotators with no axial spin. The orientations of their respective axes of symmetry relative to a reference system fixed in space may be described by spherical coordinates $\vartheta_1$, $\varphi_1$ and $\vartheta_2$, $\varphi_2$. The relative coordinates of the molecular centers of gravity may be denoted by $x$, $y$, $z$, with the Laplacian operator $\Delta$. The Hamiltonian operator is given by

$$H=-h^2\{(1/2m)\Delta+\sum_{k=1}^{2}(1/2J_k)L_k^2\}+V_n(q), \qquad L_k=\mathbf{s}_{\vartheta_k}\frac{\partial}{\partial\vartheta_k}+\frac{\mathbf{s}_{\varphi_k}}{\sin\vartheta_k}\frac{\partial}{\partial\varphi_k}, \tag{14a}$$

$$L_k^2=\frac{1}{\sin\vartheta_k}\frac{\partial}{\partial\vartheta_k}\left(\sin\vartheta_k\frac{\partial}{\partial\vartheta_k}\right)+\frac{1}{\sin^2\vartheta_k}\frac{\partial^2}{\partial\varphi_k^2},$$

[8] See for example N. Wiener, *Generalized Harmonic Analysis* (8), Acta Mathematica **55** (1930).

where $h$ is Planck's constant divided by $2\pi$, $m$ is the reduced mass of the pair, $J_1$ and $J_2$ the moments of inertia of the respective molecules and $s_\vartheta$ and $s_\varphi$ are unit vectors. The transformation determinant is

$$\Delta_0(q) = \sin\vartheta_1 \sin\vartheta_2 \tag{14b}$$

and the region $\Omega$ is given by

$$\Omega\begin{cases} -\infty \leq x, y, z \leq +\infty \\ 0 \leq \vartheta_1, \vartheta_2 \leq \pi \\ 0 \leq \varphi_1, \varphi_2 \leq 2\pi. \end{cases} \tag{14c}$$

The sum of states $\sigma_n$ of the pair of molecules is given by Eq. (13), when $H$, $\Delta_0(q)$ and $\Omega$ are taken from Eqs. (14a), (14b) and (14c).

The evaluation of the integral on the right-hand side of Eq. (13) depends upon a determination of the following functions,

$$w = e^{-\beta H}\Delta_0(q)^{-\frac{1}{2}} e^{i\mathbf{p}\cdot\mathbf{q}/h}, \tag{15}$$

which satisfy the Bloch equation

$$Hw + \partial w/\partial\beta = 0; \qquad \lim_{\beta=0} w = \Delta_0(q)^{-\frac{1}{2}} e^{i\mathbf{p}\cdot\mathbf{q}/h}. \tag{16}$$

In order to obtain an approximate solution of this equation we let

$$w = \Delta_0(q)^{-\frac{1}{2}} e^{i\mathbf{p}\cdot\mathbf{q}/h} e^{-\beta(T+V_n)} g, \tag{17}$$

where $T$ is the classical kinetic energy

$$T = \mathbf{p}_0^2/2m + \sum_{k=1}^{2} \frac{1}{2J_k}\left[p_{\vartheta k}^2 + \frac{p_{\varphi k}^2}{\sin^2\vartheta_k}\right], \qquad p_0 = p_x\mathbf{s}_x + p_y\mathbf{s}_y + p_z\mathbf{s}_z. \tag{18}$$

Substitution of (18) into the differential Eq. (16) and transformation into an integral equation with the aid of the boundary condition for $\beta = 0$, gives

$$g = 1 + ih\int_0^\beta e^{E\xi} K_1(ge^{-E\xi})d\xi + h^2\int_0^\beta e^{E\xi} K_2(ge^{-E\xi})d\xi, \tag{19}$$

$$E = T + V_n,$$

$$K_1 = \frac{1}{m}\mathbf{p}_0\cdot\Delta + \sum_{k=1}^{2}\mathbf{p}_k'\cdot L_k/J_k$$

$$K_2 = \frac{1}{2m}\Delta + \sum_{k=1}^{2}\frac{1}{2J_k}\left[L_k^2 - \cot\vartheta_k\frac{\partial}{\partial\vartheta_k} + \frac{1+\mathrm{cs}\,c^2\vartheta_k}{4}\right],$$

$$\mathbf{p}_k' = p_{\vartheta k}\mathbf{s}_{\vartheta k} + p_{\varphi k}\mathbf{s}_{\varphi k}/\sin\vartheta_k.$$

Solution by successive approximations gives

$$g = \sum_{l=0}^{\infty} g_l h^l, \qquad g_0 = 1, \qquad g_1 = i\int_0^\beta e^{E\xi} K_1(e^{-E\xi})d\xi, \tag{20}$$

$$g_l = \int_0^\beta e^{E\xi}\{K_1(e^{-E\xi}g_{l-1}) + K_2(e^{-E\xi}g_{l-2}\}d\xi.$$

The chief difference between Eq. (19) and a similar equation for translational motion alone, which

was obtained in a previous article, lies in the fact that the kinetic energy $T$ is a function of the coordinates and therefore is not a characteristic value of the kinetic energy operator.

The first three terms of the series (20) may be calculated without a great amount of labor. When they are inserted in Eqs. (18) and (15) and the indicated momentum integrations are carried out, the term proportional to $h$ vanishes and one obtains

$$\sigma_n=\left(\frac{m}{2\pi\beta h^2}\right)^{\frac{3}{2}}\frac{J_1J_2}{(2\pi\beta h^2)^2}\int_v\int_0^{2\pi}\cdots\int_0^{\pi}e^{-\beta V_n}\left[1+\sum_{k=1}^{2}\frac{\beta h^2}{6J_k}+\chi(V_n)+\cdots\right]\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 d\varphi_1 d\varphi_2 dx dy dz,$$

$$\chi=-\frac{\beta^2h^2}{12}\left\{\sum_{k=1}^{2}\frac{1}{J_k}\left[L_k^2(V_n)-\frac{\beta}{2}(L_k(V_n))^2\right]+\frac{1}{m}\left[\Delta V_n-\frac{\beta}{2}(\nabla V_n)^2\right]\right\}. \tag{21}$$

To this approximation the quantum corrections for the rotational and translational parts of the motion are additive. It should perhaps be mentioned here that the integration over the relative coordinates is effectively limited to the volume of the containing vessel $v$, by replacing the walls by high potential barriers which cause $e^{-\beta V}$ to vanish. The kinetic part of the sum of states for free rotation and translation may be written

$$\sigma_p=\left(\frac{m}{2\pi\beta h^2}\right)^{\frac{3}{2}}\prod_{k=1}^{2}\frac{2J_k}{\beta h^2}\left(1+\frac{\beta h^2}{6J_k}+\cdots\right). \tag{22}$$

If we let $\sigma_n=\sigma_p\sigma_q$ and neglect terms of the order $h$,[4] we find

$$\sigma_q=\frac{1}{16\pi^2}\int_v\int_0^{2\pi}\cdots\int_0^{\pi}e^{-\beta V_n}[1+\chi(V_n)]\sin\vartheta_1\sin\vartheta_2\, d\vartheta_1\cdots d\varphi_2 dv. \tag{23}$$

The factor $\sigma_p$ makes a contribution to the heat content but not to the pressure of the system. If the gas is made up of identical molecules and the equation of state is written in the virial form

$$pv/RT=1+(B/v)+\cdots, \tag{24}$$

where $p$ is the pressure and $R$ is the gas constant per mol, one can show by the usual arguments that

$$B=\frac{N}{32\pi^2}\int_v\int_0^{2\pi}\cdots\int_0^{\pi}[1-e^{-\beta V_n}(1+\chi(V_n))]\sin\vartheta_1\sin\vartheta_2\, d\vartheta_1\cdots d\varphi_2\, dv, \tag{24a}$$

where $N$ is Avogadro's number. If the quantum correction is small, as it usually is except at very low temperatures, Eq. (24) reduces effectively to the familiar classical expression for the second virial coefficient, containing the intermolecular potential $V_n$ from Eq. (2).

## IV.

We now return to a more detailed discussion of the intermolecular potential $V_n$ given by Eq. (2). Let us suppose that $\psi_n^0$ and $\psi_k^0$ are the unperturbed high frequency wave functions of the two molecules, referred to their respective principal axes. For fixed orientations of the molecular axes and fixed positions of their centers of gravity, the unperturbed wave function of the system with neglect of exchange degeneracy is $\psi_n^0\psi_k^0$. Properly, one should build up the wave function by linear combination of the products of the individual electron wave functions of the two molecules. Partially to remedy this defect we assume that a short range repulsive potential, arising from electron exchange and interpenetration, may be added to the van der Waals potential $V_{nk}$ calculated with

the aid of the product wave function $\psi_n{}^0\psi_k{}^0$ and we concern ourselves here only with this latter part.

The mutual electrostatic energy of the two molecules may be expanded in spherical harmonics. We assume that the molecules are neutral and that the electric center and mass center of each coincide. If $R$ is the length and $\mathbf{s}$ is a unit vector parallel to the line joining the centers of gravity of the molecules, one obtains, neglecting multipoles of higher order than the dipole

$$V(x, q) = 1/R^3[\mu_1 \cdot \mu_2 - 3(\mu_1 \cdot \mathbf{s})(\mu_2 \cdot \mathbf{s})], \quad (25)$$

where $\mu_1$ and $\mu_2$ are the electric moments of the molecules. Suppose that $\gamma_1{}^{(l)}$ and $\gamma_2{}^{(r)}$ are unit vectors in the direction of the principal optical axes and $\mu_1{}^{(l)}$ and $\mu_2{}^{(r)}$ are the components of the electric moments of the respective molecules along these axes. Then from Eqs. (2) and (25), one may write

$$V_{nk}(q) = \sum_{l,r=1}^{3} V_{nk}{}^{(lr)}$$

$$V_{nk}{}^{(lr)} = \frac{\mu_{nn}{}^{(l)}\mu_{kk}{}^{(r)}}{R^3} F_{lr}(s) - \frac{1}{R^6}\left\{\frac{\alpha_n{}^{(l)}\mu_{kk}{}^{(r)2} + \alpha_k{}^{(r)}\mu_{nn}{}^{(l)2}}{2} + \sum_{\substack{n' \neq n \\ k' \neq k}} \frac{|\mu_{n'n}{}^{(l)}|^2 |\mu_{k'k}{}^{(r)}|^2}{(E_{n'}{}^0 + E_{k'}{}^0) - (E_n{}^0 + E_k{}^0)}\right\} F_{lr}(s)^2, \quad (26)$$

$$F_{lr}(s) = \gamma_1{}^{(l)} \cdot \gamma_2{}^{(r)} - 3(\gamma_1{}^{(l)} \cdot \mathbf{s})(\gamma_2{}^{(r)} \cdot \mathbf{s}).$$

Since the diagonal matrix elements $\mu_{nn}$ and $\mu_{kk}$ are merely the average values of the dipole moments, the first term of Eq. (26) is the mutual electrostatic energy of the permanent electric moments of the two molecules. The second term, arising from states $(n'k)$ and $(nk')$, corresponds to an interaction of the low frequencies of the one molecule with the high frequencies of the other. For these terms the summations in Eq. (2) may be carried out to give one-half the electrostatic polarizabilities $\alpha_n{}^{(l)}$ and $\alpha_k{}^{(r)}$ of the ground states of the respective molecules. Since we have chosen the principal axes, the polarizability tensor of each molecule is diagonal. The third part of Eq. (26) involves only the high frequency terms $(n'k')$. For molecules without permanent dipoles, Eq. (26), when averaged over molecular orientations by means of the formula

$$\overline{F_{lr}{}^2(s)} = 2/3 \quad (27)$$

reduces to London's formula for the van der Waals energy, averaged over all values of the space quantum numbers.

The usefulness of the semiclassical potential (26) in statistical calculations depends upon whether the quantum correction $\chi(V)$ which must be applied to the sum of states, Eqs. (21) and (23), is small. To obtain an estimate of the quantum correction, we consider two identical diatomic molecules with permanent dipole moments $\mu$ directed along their respective axes of symmetry. The first term of Eq. (26) becomes in this case

$$V = (\mu^2/R^3)[\gamma_1 \cdot \gamma_2 - 3(\gamma_1 \cdot s)(\gamma_2 \cdot s)], \quad (28)$$

where $\gamma_1$ and $\gamma_2$ are unit vectors in the direction of the symmetry axes. The remaining terms may be expressed as functions of $\gamma_1$, $\gamma_2$, $\mathbf{s}$ by means of the following relations, which may be easily verified from the orthogonality conditions for direction cosines.

$$\sum_{l=1}^{3} F_{lr}(s)^2 = 1 + 3(\gamma_2{}^{(r)} \cdot \mathbf{s})^2; \quad \sum_{l,r=1}^{3} F_{lr}(s)^2 = 6. \quad (29)$$

The expressions are rather cumbersome and will not be written down here. The translational quantum correction and the rotational quantum correction arising from the optical anisotropy will usually be small relative to the dipole-dipole quantum correction associated with the potential (28). We therefore calculate only this latter correction by means of Eq. (21). The Laplacian and gradient operators are of course independent of the orientation of the reference system. Making use of Eq. (21) and the relations

$$L_k^2(\mathbf{a}\cdot\gamma_k)=-2(\mathbf{a}\cdot\gamma_k),$$
$$L_k(\mathbf{a}\cdot\gamma_k)=\mathbf{a}-\gamma_k(\mathbf{a}\cdot\gamma_k), \tag{30}$$

where $\mathbf{a}$ and $\gamma_k$ are any two independent unit vectors, one obtains for the quantum correction

$$\chi=\frac{\beta^2\mu^2h^2}{3R^3}\left\{\frac{A_1}{J}+\frac{\beta\mu^2}{R^3}\left[\frac{A_2}{J}+\frac{A_3}{mR^2}\right]\right\},$$

$$A_1=\gamma_1\cdot\gamma_2-3(\gamma_1\cdot\mathbf{s})(\gamma_2\cdot\mathbf{s}),$$
$$A_2=\tfrac{1}{4}[1+(3/2)[(\gamma_1\cdot\mathbf{s})^2+(\gamma_2\cdot\mathbf{s})^2]-A_1^2], \tag{31}$$
$$A_3=(9/8)\{A_1[A_1-2(\gamma_1\cdot\mathbf{s})(\gamma_2\cdot\mathbf{s})]+(\gamma_1\cdot\mathbf{s})^2$$
$$+(\gamma_2\cdot\mathbf{s})^2+2(\gamma_1\cdot\gamma_2)(\gamma_1\cdot\mathbf{s})(\gamma_2\cdot\mathbf{s})\}.$$

The third term of (31) may be ignored for the present, since $mR^2$ is usually much larger than $J$. Maximum interaction occurs when the two dipoles are oriented parallel to $s$. Here we find

$$|\chi|=\tfrac{2}{3}(\beta^2\mu^2h^2/R^3J). \tag{32}$$

For a typical polar molecule, HCl, $\mu=1.03\times10^{-18}$ e.s.u. and $J=2.65\times10^{-40}$ g cm$^2$. In this case $\chi=1.56\times10^4/R^3T^2$ where $R$ is expressed in Angstrom units. Thus at 300° Kelvin with a separation of 3A, a reasonable value for the distance of closest approach of two HCl molecules in thermal collisions, $\chi=0.06$. Since this is still fairly small relative to unity, it seems possible to conclude that the classical phase integral remains a good approximation at ordinary temperatures.

It will be recalled that the integrand in the expression (23) for $\sigma_q$ is also the configuration probability (Kirkwood, reference 5). The average energy may be calculated by means of the formula

$$\bar{V}=(\int Ve^{-\beta V}(1+\chi)dq)/(\int e^{-\beta V}(1+\chi)dq). \tag{33}$$

If $e^{-\beta V}$ is expanded and the average taken over all molecular orientations, one obtains, neglecting inverse powers of $R$ higher than the sixth:

$$\bar{V}=-\frac{2}{3}\frac{\beta\mu^4}{R^6}\left(1-\frac{\beta h^2}{3J}\right)-\frac{2\bar{\alpha}\mu^2}{R^6}$$
$$-\frac{6}{R^6}\sum_{\substack{n\neq n\\ k,\,n}}\frac{\overline{|\mu_{n'n}|^2}\,\overline{|\mu_{n''n}|^2}}{E_{n'}^0+E_{n''}^0-2E_n^0},$$

$$\bar{\alpha}=(\alpha_x+\alpha_y+\alpha_z)/3,$$

$$\overline{|\mu_{n'n}|^2}=[|\mu_{n'n}{}^{(x)}|^2+|\mu_{n'n}{}^{(y)}|^2+|\mu_{n'n}{}^{(z)}|^2]/3. \tag{34}$$

It should be remarked that this expansion is not a particularly good approximation for equation of state calculations, since $\beta\mu^2/R^3$ may not be small. However, it serves to illustrate the relative magnitudes of different contributions to the intermolecular energy. The first term corresponds to the Richt effect of Keesom.[9] Except for the small quantum correction, it has its classical value. The quantum correction $\beta h^2/3J$ is exactly twice that which must be applied to the electric susceptibility of a molecule. Thus, if terms of the order $h^4$ are neglected, it is seen that a dipole molecule at high temperatures has the same effective mean square moment whether interacting with the field of another dipole molecule or with an external electric field. The second term of Eq. (34) corresponds to the induction effect of Falkenhagen[1] and the third to the high frequency dispersion effect of London.[2] At ordinary temperatures, the first and third terms of Eq. (34) are of the same order of magnitude for typical polar molecules, while the second term is relatively small. At very high temperatures the influence of the first term becomes small but at low temperatures it becomes predominant.

At a later time, an attempt will be made to apply the present considerations to a calculation of the equations of state of polar molecules. It should be remarked that a calculation of the

[9] W. H. Keesom, Phys. Zeits. **22**, 129, 643 (1921).

van der Waals $A$ constant is not sufficient. Thus it is impossible to represent the second virial coefficient of a polar gas by $b_0 - A/RT$, except over a very short temperature range. The experimental $A$ constants have, therefore, no clear cut theoretical significance.

From the foregoing discussion it seems possible to conclude that the sum of states of a gas at ordinary temperatures is closely approximated by the classical Gibbs phase integral. The approximation may be improved by including a quantum correction, Eq. (21), which is usually very small except at quite low temperatures. The semiclassical potential Eq. (26), from which all low frequency quantum numbers have been eliminated, is to be employed in the calculation of the phase integral. The low frequency contributions to the intermolecular energy have essentially their classical values and the high frequency contribution is given by a modification of London's formula, in which continuous functions of the molecular orientations appear in the place of space quantum numbers.

*Note added in Proof:* If rectangular coordinates are employed the sum of states of a particle is given by[5]

$$\sigma = (2\pi\hbar)^{-1} \int \cdots \int e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} e^{-\beta H} \times e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} dx dy dz dp_x dp_y dp_z \quad \text{(a)}$$

where $\mathbf{p}$ is the momentum and $\mathbf{r}$ is the radius vector of the particle. To express this integral in terms of generalized coordinates, one would most simply express $\mathbf{p}\cdot\mathbf{r}$ and $H$ in terms of the new $p$'s and $q$'s and replace $dx \cdots dp_z$ by the product of the differentials of the new $p$'s and $q$'s, since the transformation determinant in phase space is unity. However, this procedure is not convenient in the case of rigid rotor. If the rotor is represented by a mass point moving on the surface of a sphere, one sees that $\mathbf{p}\cdot\mathbf{r}$ vanishes and the integrand of (a) becomes indeterminate. For this reason it is necessary to resort to the method of Section III, in which the transformation determinate of the $q$'s appears. Due to the uncertainty principle, quantum mechanics does not uniquely determine a probability distribution function in phase space, $P(p, q)$, but only integrated distribution functions $\overline{P}(q)$ and $\overline{P}(p)$ in configuration or in momentum space. Thus there is a certain amount of flexibility in the choice of the integrand employed in the representation of $\sigma$.

# The Nature of the Chemical Bond. VI. The Calculation from Thermochemical Data of the Energy of Resonance of Molecules Among Several Electronic Structures[1]

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In the first part of this paper there is given a set of bond-energy values for single, double, and triple bonds between atoms, obtained from thermochemical data, such that the total energy of formation from separate atoms of a molecule containing given bonds is equal to the sum of the energies for those bonds. In the derivation of these values data were used only for molecules for which it is probable that one electronic structure, corresponding to one distribution of valence bonds, represents the normal state to a satisfactory degree of approximation. For other molecules more than one electronic structure of this type contributes essentially to the normal state, the energy of formation of the molecule then being larger than that for any one of the contributing structures. On comparing the energies of formation given by thermochemical data with the values calculated for various structures, it is verified that this difference is always positive or zero (to within the limits of error involved). The difference in energy is interpreted as the resonance energy of the molecule among several electronic structures, and its existence in a given case provides strong evidence that more than one structure is contributing to the normal state of the molecule, the number and importance of the contributing structures being indicated by the magnitude of the resonance energy. In this way the existence of resonance is shown for many molecules, and values found for the resonance energy are tabulated. The substances discussed include carbon dioxide, carbon disulfide, alkyl isocyanates, carboxylic acids and esters, aliphatic amines, carbonic esters, urea and related substances, benzene and benzene derivatives, naphthalene and other condensed ring systems, pyridine and related heterocyclic compounds, biphenyl, fluorene, phenylethylene, dihydronaphthalene, quinone, some ureides and purines, etc.

## INTRODUCTION

IT has been recently recognized that molecules can be divided roughly into two classes, the first comprising those for which the normal electronic state can be reasonably well approximated by an eigenfunction corresponding to a single electronic structure of the Lewis type; that is, to a single distribution of valence bonds, and the second those for which the normal electronic state can be satisfactorily represented only by a linear combination of several such eigenfunctions. A molecule belonging to this second class is said to resonate among the corresponding electronic structures. Information as to the classification of a given molecule may be obtained from the consideration of theoretical or empirical energy curves,[2] from the comparison of observed interatomic distances with the sum of atomic radii,[3] and in other ways. In particular the comparison of the energy of the molecule with the values corresponding to various electronic structures should provide a valuable criterion, inasmuch as the energy of the normal molecule must be equal to or less than the energy for any electronic structure. If more than one of the reasonable electronic structures for a molecule correspond to nearly the same energy value, which is somewhat higher than the actual energy of the molecule, the difference in energy may be confidently interpreted as the resonance energy of the molecule among these electronic structures. Assuming that the total energy of formation of a nonresonating molecule from separated atoms may be represented as the sum of bond energies, we in this work have calculated values of the energies of various single, double, and triple bonds from thermochemical data. With the use of these we have then predicted energies for various electronic structures for other molecules, and have in this way shown the existence of resonance and have calculated values of the resonance energy for a large number of substances, including in particular carboxylic acids, amides, and other compounds with a resonating

[1] The fifth paper of this series appeared in J. Chem. Phys. **1**, 362 (1933).

[2] L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932).

[3] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293, 498 (1932).

double bond, aromatic hydrocarbons and their derivatives, heterocyclic compounds, etc.

It has been pointed out[4] that bonds between non-identical atoms may be considered to resonate between a covalent and an ionic structure, the bond in this way having partially covalent and partially ionic character. The resonance energy of this effect, which is usually essentially the same for a given bond in different molecules, is included in the values given for the bond energies in the nonresonating molecules discussed.

Although much of the body of thermochemical data which we use has been available for a long time, and many attempts at interpreting it by the introduction of the concept of bond energies have been made, the derivation of a satisfactory set of essentially constant bond energies was not made earlier because the necessity of using a restricted class of molecules was not recognized. It remained for the quantum mechanics to indicate the possibility of resonance of some molecules among several structures corresponding to different distributions of valence bonds, with a consequent change in total energy, and to suggest the determination of bond energies by the consideration of only those molecules for which a single electronic structure can be written with considerable confidence.

## Bond Energies in Molecules Represented by a Single Electronic Structure

In formulating a set of bond-energy values we first calculated the energies of formation of molecules from experimental values of the heats of combustion of the compounds[5] and thermochemical data pertaining to the products of combustion—carbon dioxide, water, nitrogen, etc. The same values for the latter quantities were used as previously.[4]

Throughout this paper the unit of energy is the volt-electron (1 v.e. = 23.054 kcal.). The symbol A−B denotes a single bond between the atoms A and B, A=B a double bond, etc. The letter $E$ represents the heat of formation of the gaseous substance at 25°C from widely separated atoms, the energy of the substance (except for small $pv$ terms) being equal to $-E$.

In a previous discussion[4] it was pointed out that there is some arbitrariness in the choice of bond energies, arising from uncertainty in the experimental data, lack of constancy of bond energies from compound to compound, and other causes. Because of differences in the data used and their treatment, the values given in that paper and the present one differ somewhat; the difference in no case exceeds 0.1 v.e., however, which is of the order of magnitude of the errors inherent in the data.

The bond-energy values obtained in this way[6] are given in Table I. It is noteworthy that the energy of a given bond may in some cases change somewhat from one compound to another of different type; thus the C=O bond energy is considerably changed as hydrogen attached to the carbon atom under consideration is replaced by aliphatic radicals. This effect is probably due in the main to interactions of bonds from the same atom, inasmuch as it is especially pronounced for bonds (such as C−O, C=O, C≡N) with which large electric dipole moments are associated. In default of a thorough understanding of the phenomenon, we have contented ourselves with using for each substance values of bond energies obtained from substances resembling it.

Table I. *Bond energies.*

| Bond | Energy | Source |
|---|---|---|
| C−H | 4.323 v.e. | Methane |
| N−H | 3.895 | Ammonia |
| O−H | 4.747 | Water |
| C−C | 3.65 | Paraffins |
| C=C | 6.56 | Olefins and Cyclic Compounds |
| C≡C | 8.61 | Acetylene Hydrocarbons |
| N−N | 1.44 | Reference 4 |
| C−O | 3.47 | Aliphatic Primary Alcohols |
| | 3.59 | Aliphatic Ethers |
| C=O | 7.20 | Formaldehyde |
| | 7.56 | Other Aldehydes |
| | 7.71 | Ketones |
| C−N | 2.95 | Amines |
| C=N | 5.75 | Estimated Value |
| C≡N | 8.75 | Hydrogen Cyanide |
| | 9.07 | Aliphatic Cyanides |
| C−S | 2.92 | Mercaptans and Thio-ethers |
| C=S | 5.60 | Estimated Value |

[4] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[5] The heats of combustion used were taken from Kharasch's compilation (Bur. Standards J. Research **2**, 359 (1929)) or from Landolt-Börnstein Tables.

[6] The detailed discussion of the derivation of these values is omitted for the sake of brevity.

The surprisingly large value of the C=O bond is no doubt associated with the possibility of writing for $R_2CO$ the structure $R_2=\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ as well as $R_2=C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, the former "semipolar" structure contributing an appreciable resonance energy. The magnitude of this contribution might be especially easily influenced by adjacent groups, the presence of hydrogen attached to the carbon atom having a pronounced effect in inhibiting it.

## Resonance Energies of Carbon Dioxide, Alkyl Isocyanates, etc.

In calculating the resonance energy of a molecule, we write for the molecule the electronic structure corresponding to the usually accepted distribution of valence bonds, and calculate the corresponding value of $E'$ by summing the bond energies, using values from similar compounds in case more than one bond energy is given in Table I. The difference between the experimental value of $E$ and the calculated value of $E'$ is interpreted as resonance energy resulting from contributions of other electronic structures to the normal state of the molecule. This treatment is applicable at present only to molecules for which stable structures can be written involving neutral atoms only; compounds such as $HN_3$, with the structure $H:\overset{\cdot\cdot}{N}::\overset{+}{N}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:^{-}$ making the largest contribution to the normal state, cannot be discussed until methods are developed for evaluating the energies of partially ionic bonds.

Evidence from interatomic distances[3] has shown the existence of resonance in CO, $CO_2$, $CS_2$, RNCO, and many other simple molecules. This is supported by the consideration of the energy of these molecules. The value of $E$ for CO is 11.30 v.e., 3.59 v.e. greater than the ketone value for C=O. This very large difference has already been accounted for[3] as resulting from the great stability of the structure $:\overset{-}{C}:::\overset{+}{O}:$, whose contribution to the eigenfunction for the normal state is even larger than that of $:C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$.

Carbon dioxide, with $E=16.79$ v.e., has a resonance energy of 1.37 v.e. relative to the structure $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}=C=\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, with the ketone C=O value. This large resonance energy is due to the structures $:\overset{+}{O}:::C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ and $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}C:::\overset{+}{O}:$, direct evidence for which is provided by the observed interatomic distances. The molecules SCO, with $E=14.55$ v.e., and $CS_2$, with $E=12.46$ v.e., have resonance energies of 0.84 v.e. and 0.46 v.e., respectively.

The values $E=29.64$ v.e. for methyl isocyanate and $E=41.99$ v.e. for ethyl isocyanate correspond to resonance energies of 0.26 v.e. and 0.31 v.e., respectively, relative to the structure $R:\overset{\cdot\cdot}{N}=C=\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$. The other structures contributing to the normal state are no doubt the same as in $CO_2$. Methyl isothiocyanate, $CH_3NCS$, with $E=28.10$ v.e., has a resonance energy of 0.43 v.e.

The value $E=20.01$ v.e. for cyanamide leads to a resonance energy of 0.20 v.e. relative to the structure $H_2N-C\equiv\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:$, which is without doubt due to resonance with $H_2\overset{+}{N}=C=\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:^{-}$.

It should be emphasized that the resonance energies calculated by the use of bond energies such as C=O from ketones do not include the energy of resonance between $C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$ and $\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$. For example, if we were to assign to $C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, that is, the normal covalent carbon-oxygen double bond, the estimated bond energy 6.60 v.e., then the ketones would show a resonance energy of 1.11 v.e. arising from the $R_2=\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ structure, and carbon dioxide a total resonance energy of 3.59 v.e. The procedure of using ketone C=O, etc., bond energies rather than the normal covalent energies has been adopted for two reasons. First, there is no satisfactory way of determining the value of $C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, for in no molecule is resonance to $\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ prohibited. Second, since in every molecule con-

taining C=O there is resonance between $C::\ddot{O}:$ and $\overset{+}{C}:\ddot{O}:^{-}$, it must always be considered in interpreting the total resonance energy, and this is most easily done by simply using a C=O bond energy which already includes this resonance energy.

## Resonance Energies of Aliphatic Acids, Esters, Amides, and Related Compounds

### Carboxylic acids and esters

Data for acetic acid and eight other monobasic acids lead to a value of 1.20 v.e. for the resonance energy of the carboxyl group relative to the structure $R-C(=O)-OH$, with the use of the ketone value for C=O. Data for eight dibasic carboxylic acids lead to the value 1.19 v.e. per carboxyl group, in excellent agreement with the monobasic acid value.

In the carboxylic anions there is complete degeneracy between the structures $R-C(=O)-O^{-}$ and $R-C(-O^{-})=O$, so that appreciable energy of resonance between these two structures may well be expected. We have not obtained any empirical data for these ions. The extent to which the resonance is inhibited by attaching hydrogen to one of the two previously equivalent oxygen atoms cannot be predicted. Our value of 1.20 v.e. for the resonance energy in the carboxylic acids is a lower limit for the resonance energy in the corresponding anions.

It is to be expected from chemical evidence that the replacement of hydrogen by an aliphatic radical would have some further inhibiting effect on the carboxyl resonance. It is found, however, that to within the experimental error of about 0.2 v.e. the resonance energy is the same for methyl and ethyl esters as for carboxylic acids.

### Aliphatic amides

The values $E=23.55$ v.e. for formamide, $HCONH_2$, and 35.96 v.e. for acetamide, $CH_3CONH_2$, lead to a resonance energy of 0.93 v.e. and 0.89 v.e., respectively, calculated relative to the structure

$$R-C(=O)-NH_2.$$

The expected resonance is between this structure and the structure

$$R-C(-O^{-})=\overset{+}{N}H_2,$$

and the value 0.9 v.e. obtained is not greatly different from the related value 1.20 v.e. for the carboxyl group.

Oxamide, $(CONH_2)_2$, with $E=42.60$ v.e., has a total resonance energy of 2.05 v.e., or 1.03 v.e. per amide group, in agreement with the above value. Oxamic acid, $COOH\cdot CONH_2$, with $E=40.12$ v.e., has a total resonance energy of 1.99 v.e., nearly the sum of the values for the carboxyl group in oxalic acid and for the amide group in oxamide.

### Carbonic esters, urea, etc.

In the carbonate ion,

$$\bar{O}-C(=O)-\bar{O},$$

guanidonium ion,

$$H_2N-C(=\overset{+}{N}H_2)-NH_2,$$

etc., there is complete degeneracy of the three structures corresponding to the three positions of the double bond, so that a resonance energy considerably larger than that in the carboxyl group is anticipated. Data on these symmetrical ions are not available, but data for similar unsymmetrical compounds, discussed below, in which resonance is only partially inhibited by the incomplete degeneracy lead to resonance energies of about 1.8 v.e.

Dimethyl carbonate, with $E=49.81$ v.e., and diethyl carbonate, with $E=74.46$ v.e., lead to a

carbonate resonance energy of 1.78 v.e. and 1.83 v.e., respectively. Urea, $CO(NH_2)_2$, with $E=30.78$ v.e., and urethane, $C_2H_5OCONH_2$, with $E=52.79$ v.e., have resonance energies of 1.59 v.e. and 1.89 v.e., respectively. No thermal data are available for guanidine.

## The Aromatic Hydrocarbons

### Benzene

The value of $E'$ calculated for one of the Kekulé structures for benzene, $E'=6C-H+3C-C+3C=C$, is 56.58 v.e. The data given in Table II for benzene and five other compounds lead to an average resonance energy between the two equivalent Kekulé structures, together with the additional contributions of the three excited states,[7] of 1.71 v.e.

Table II. *Benzene and benzene derivatives.*

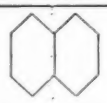
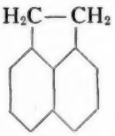
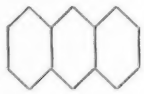
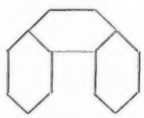
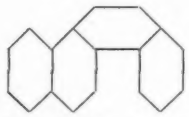
| Compound | Formula | $E$ | $E'$ | Resonance energy |
|---|---|---|---|---|
| Benzene | $C_6H_6$ | 58.20 | 56.58 | 1.62 v.e. |
| Toluene | $C_6H_5CH_3$ | 70.58 | 68.88 | 1.70 |
| Ethylbenzene | $C_6H_5C_2H_5$ | 82.90 | 81.18 | 1.72 |
| Propylbenzene | $C_6H_5C_3H_7$ | 95.27 | 93.48 | 1.79 |

The values of $E'$ and $E$ can be estimated from their internal consistency to be accurate to about $\pm 0.1$ v.e., the value of 1.71 v.e. for the resonance energy being accurate to about $\pm 0.15$ v.e. The quantum mechanical discussion of resonance in benzene and naphthalene is given in the preceding paper.[1]

### Naphthalene, anthracene, and other condensed ring systems

Data given in Table III lead to resonance energies relative to the usual structures with the maximum number of double bonds between adjacent carbon atoms of 3.24 v.e. and 3.07 v.e. for naphthalene and acenaphthene, 4.54 v.e. for anthracene, 4.78 v.e. for phenanthrene, and 6.53 v.e. for chrysene. These values are roughly equal to integral multiples of 1.71 v.e., the value found for benzene, the integral factor being in each case the number of benzene rings in the condensed ring system. The deviations are always in the direction of decreased resonance, the ratios for

Table III. *Condensed ring systems.*

| Compound | Formula | Structure | $E$ | $E'$ | Resonance energy |
|---|---|---|---|---|---|
| Naphthalene | $C_{10}H_8$ |  | 92.52 | 89.28 | 3.24 |
| Acenaphthene | $C_{12}H_{10}$ |   | 111.95 | 108.88 | 3.07 |
| Anthracene | $C_{14}H_{10}$ |  | 126.54 | 122.00 | 4.54 |
| Phenanthrene | $C_{14}H_{10}$ |  | 126.78 | 122.00 | 4.78 |
| Chrysene | $C_{18}H_{12}$ |  | 161.25 | 154.72 | 6.53 |

[7] See reference 1.

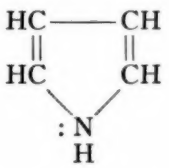
benzene and these five molecules being 1 : 1.90 : 1.80 : 2.66 : 2.80 : 3.82.

The saturated side ring in acenaphthene should not change the resonance energy from that of naphthalene, the small discrepancy observed (3.07 v.e. as against 3.24 v.e.) being attributed to experimental error. The ratio to 1.71 v.e. for acenaphthene, 1.80, is in better agreement with the quantum-mechanical ratio 1.82 than is the ratio 1.90 found for naphthalene itself, though in both the disagreement is within the experimental error.

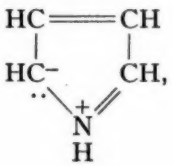
### Heterocyclic Compounds

Data are given in Table IV for heterocyclic compounds. For piperidine there is no difference between $E$ and $E'$, showing that the bond energies used are applicable to saturated heterocyclic molecules. Pyridine and quinoline differ from benzene and naphthalene only by the presence of one N in place of CH; and, as expected, the values 1.87 v.e. and 3.01 v.e., respectively, of the resonance energy are equal to within 10 percent to the values for the corresponding hydrocarbons.

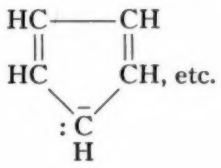
Pyrrole, $C_4H_5N$, is found to have a resonance energy of 0.98 v.e., despite the fact that the structure



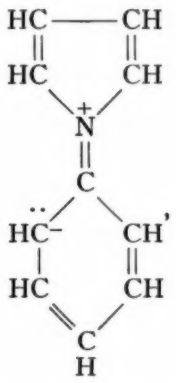
is the only structure that can be written for it in which each carbon atom forms four bonds with adjacent atoms. The large resonance energy requires that other structures contribute strongly to the normal state of this molecule. The most reasonable additional structures that can be written are the four of the type



which differ from the first in that the two double bonds are shifted and the unshared electron pair is on carbon rather than nitrogen. A negative carbon atom, with one unshared and three shared electron pairs, occurs rather often in resonating structures, as in carbon monoxide, the negative hydrocarbon free radicals, the ion $C_5H_5^-$ (in the alkali salts of pentadiene), which resonates among the five equivalent structures



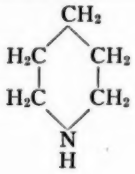
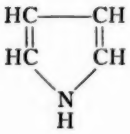
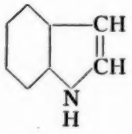
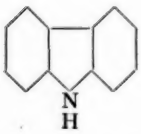
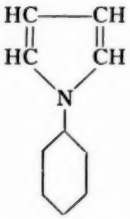
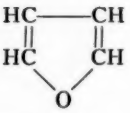
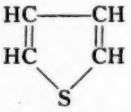
Indole, $C_8H_7N$, and carbazole, $C_{12}H_9N$, have resonance energies of 2.34 v.e. and 3.93 v.e., respectively, 0.63 v.e. and 0.51 v.e. greater than for the benzene rings in the indicated structures. For indole we expect the resonance energy to be somewhat smaller than the sum for benzene and pyrrole, because of the suppression of resonance from the sharing of two atoms by the two rings; in agreement with this argument, the observed value is 0.35 v.e. less than the sum $1.71+0.98=2.69$ v.e. Similarly for carbazole the observed resonance energy is 0.47 v.e. less than the sum $2\times1.71+0.98=4.40$ v.e. The resonance energy of phenylpyrrole, 3.29 v.e., is 0.60 v.e. greater than the sum of the pyrrole and benzene resonance energies; this additional stability is due to structures such as



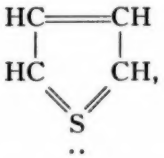
in which the unshared electron pair is on a carbon atom ortho or para to nitrogen.

The resonance energy of 0.93 v.e. for furane, $C_4H_4O$, arises from the same structures as for pyrrole.

TABLE IV. *Resonance energies of heterocyclic compounds.*

| Compound | Formula | Structure | *E* | *E'* | Resonance energy |
|---|---|---|---|---|---|
| Piperidine | $C_5H_{11}N$ |  | 67.58 | 67.60 | — |
| Pyridine | $C_5H_5N$ | | 52.61 | 50.74 | 1.87 |
| Quinoline | $C_9H_7N$ | | 86.46 | 83.45 | 3.01 |
| Pyrrole | $C_4H_5N$ |  | 44.84 | 43.86 | 0.98 |
| Indole | $C_8H_7N$ |  | 78.91 | 76.57 | 2.34 |
| Carbazole | $C_{12}H_9N$ |  | 113.22 | 109.29 | 3.93 |
| Phenylpyrrole | $C_{10}H_9N$ |  | 98.45 | 95.16 | 3.29 |
| Furane | $C_4H_4O$ |  | 42.18 | 41.25 | 0.93 |
| Thiophene | $C_4H_4S$ |  | 41.21 | 39.86 | 1.35 |

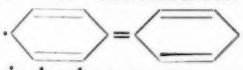
Despite its five-membered ring, thiophene, $C_4H_4S$, shows a remarkably close resemblance to benzene in its properties. The resonance energy found for it, 1.35 v.e., is to be mainly attributed to the same structures as for pyrrole, though the structure

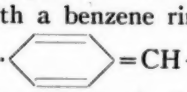


using five *M* orbits in sulfur, may make a small contribution also.

## Resonance in Conjugated Systems Containing Aromatic Nuclei

### Biphenyl and related compounds

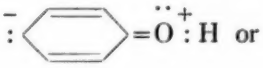
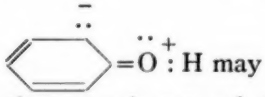
The thermochemical data for aliphatic hydrocarbons containing conjugated double bonds, such as butadiene, $CH_2=CH-CH=CH_2$, etc., are not very reliable, but suggest a value of about 0.2 v.e. for the resonance energy. The data for molecules containing aromatic rings are more reliable, and show the existence of extra resonance accompanying increase in length of a conjugated system. Thus the value 3.77 v.e. for the resonance energy of biphenyl is 0.35 v.e. larger than the resonance energy of two benzene rings, the additional resonance being attributed to the contribution of structures such as  , the dots representing single electrons on ortho or para carbon atoms. (These electrons are formally to be considered paired, in order to give a singlet state.) The resonance energy of fluorene should be the same as for biphenyl; the somewhat larger value given in Table V is probably due to error in the reported heat of combustion. For 1,3,5-triphenylbenzene, for which many quinone-type structures must be considered, the additional resonance energy is found to be 1.1 v.e.

For phenylethylene, in which a double bond conjugated with a benzene ring permits structures such as  , the additional resonance energy is 0.29 v.e., and for stilbene, with two phenyl groups conjugated with the double bond, it is 0.67 v.e. The conjugation of a triple bond and a benzene ring in phenylacetylene provides extra resonance energy to the extent of 0.45 v.e. The extra resonance energy in 1,2-dihydronaphthalene is 0.32 v.e., in good agreement with the value for phenylethylene. The extra resonance energy in furylethylene is 0.25 v.e.

### Benzene derivatives

The extra resonance energy of phenylcyanide, benzoic acid, benzaldehyde, acetophenone, and other benzene derivatives in which a double or triple bond in a side chain is conjugated with the benzene ring should be about the same as for phenylethylene. The average value for these four compounds (Table VI) is 0.21 v.e. In benzophenone the larger extra resonance energy of 0.45 v.e. results from the conjugation of C=O with the two benzene rings.

For symmetrical and unsymmetrical diphenylurea we expect some extra resonance energy in addition to that for two benzene rings and urea because of conjugation of these groups; the values found are 0.55 v.e. and 0.50 v.e., respectively.

In phenol, aniline, and other compounds in which an atom with unshared electron pairs is attached directly to the benzene ring, structures such as  or especially  may contribute appreciably to the normal state of the molecule; this is presumably the cause of the extra resonance energy of about 0.25 v.e. found for such compounds (Table VI). The high value for hydroquinone may indicate some additional resonance, the cause of which is not evident.

### The quinones

The data given in Table VII for the quinones show large extra resonance energies of 0.57 v.e. in quinone, 1.42 v.e. in anthraquinone, and 1.4 v.e. in phenanthraquinone, in addition to the resonance energy of two benzene rings in the last two compounds. These large values we attribute to structures such as ,

TABLE V. *Resonance energies of biphenyl and related compounds.*

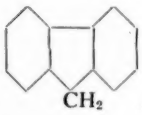
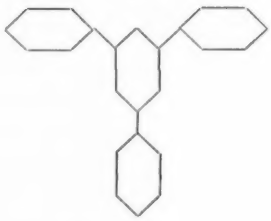
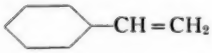
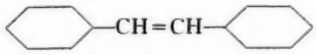
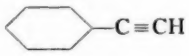
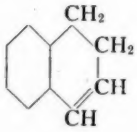
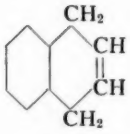
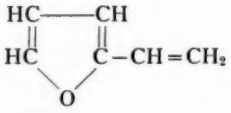
| Compound | Formula | Structure | $E$ | $E'$ | Resonance energy | Extra resonance energy |
|---|---|---|---|---|---|---|
| Biphenyl | $C_{12}H_{10}$ | | 111.91 | 108.14 | 3.77 | 0.35 |
| Fluorene | $C_{13}H_{10}$ |  | 119.57 | 115.44 | 4.13 | 0.71 |
| 1,3,5-Triphenylbenzene | $C_{24}H_{18}$ |  | 219.2 | 211.3 | 7.9 | 1.1 |
| Phenylethylene | $C_8H_8$ |  | 77.42 | 75.42 | 2.00 | 0.29 |
| Stilbene | $C_{14}H_{12}$ |  | 131.08 | 126.99 | 4.09 | 0.67 |
| Phenylacetylene | $C_8H_6$ |  | 70.99 | 68.83 | 2.16 | 0.45 |
| 1,2-Dihydronaphthalene | $C_{10}H_{10}$ |  | 97.05 | 95.02 | 2.03 | 0.32 |
| 1,4-Dihydronaphthalene | $C_{10}H_{10}$ |  | 96.73 | 95.02 | 1.71 | 0.00 |
| Furylethylene | $C_6H_6O$ |  | 61.28 | 60.10 | 1.18 | 0.25 |

TABLE VI. *Benzene derivatives.*

| Compound | Formula | $E$ | $E'$ | Resonance energy | Extra resonance energy |
|---|---|---|---|---|---|
| Phenyl cyanide | $C_6H_5CN$ | 66.89 | 64.97 | 1.92 | 0.21 |
| Benzoic acid | $C_6H_5COOH$ | 74.91 | 71.82 | 3.09 | 0.18 |
| Benzaldehyde | $C_6H_5CHO$ | 69.64 | 67.78 | 1.86 | 0.15 |
| Acetophenone | $C_6H_5COCH_3$ | 82.24 | 80.22 | 2.02 | 0.31 |
| Benzophenone | $C_6H_5COC_6H_5$ | 123.37 | 119.50 | 3.87 | 0.45 |
| Sym.-diphenylurea | $C_6H_5NH\cdot CO\cdot NHC_6H_5$ | 137.35 | 131.79 | 5.56 | 0.55 |
| Unsym.-diphenylurea | $(C_6H_5)_2N\cdot CONH_2$ | 137.30 | 131.79 | 5.51 | 0.50 |
| Phenol | $C_6H_5OH$ | 62.46 | 60.46 | 2.00 | 0.29 |
| Anisole | $C_6H_5OCH_3$ | 74.37 | 72.40 | 1.97 | 0.26 |
| Hydroquinone | $C_6H_4(OH)_2$ | 66.83 | 64.35 | 2.48 | 0.77 |
| Aniline | $C_6H_5NH_2$ | 64.89 | 62.99 | 1.90 | 0.19 |
| Methylaniline | $C_6H_5NHCH_3$ | 76.99 | 75.01 | 1.98 | 0.27 |
| Dimethylaniline | $C_6H_5N(CH_3)_2$ | 88.84 | 87.03 | 1.81 | 0.10 |
| Diphenylamine | $(C_6H_5)_2NH$ | 118.26 | 114.29 | 3.97 | 0.55 |

in which a benzene (or anthracene or phenanthrene) nucleus is formed by changing the C=O bond to a single bond, leaving an odd electron on each oxygen (the two being formally paired).

TABLE VII. *Resonance energy of quinones.*

| Compound | Formula | $E$ | $E'$ | Resonance energy | Extra resonance energy |
|---|---|---|---|---|---|
| Quinone | $C_6H_4O_2$ | 61.01 | 60.44 | 0.57 | 0.57 |
| Anthraquinone | $C_{14}H_8O_2$ | 130.54 | 125.70 | 4.84 | 1.42 |
| Phenanthraquinone | $C_{14}H_8O_2$ | 130.5 | 125.70 | 4.8 | 1.4 |

## UREIDES AND PURINES

Values of $E$ for some ureides and purines are given in Table VIII. For many of the substances it was necessary to estimate heats of vaporization or sublimation, in which cases $E$ is given only to 0.1 v.e. The values of $E'$ and the resonance energy $E-E'$ refer to the ketonic structures shown in the table; similar calculations may be easily made for enolic structures, leading usually to somewhat larger resonance energies. The ketonic resonance energies given do not include the energy of resonance of carbonyl between the structures $C::\ddot{O}:$ and $\overset{+}{C}:\ddot{O}:^{-}$, inasmuch as the ketone value C=O=7.71 v.e. was used in calculating $E'$.

The ureides hydantoin, parabanic acid, alloxan, barbituric acid, and 4-methyluracil show resonance energies of between 2.3 v.e. and 3.1 v.e., resulting from resonance of the double bonds among the various possible positions. These values seem not unreasonable when compared with the value 1.59 v.e. for urea. However, we should expect the resonance energy for hydantoin to be somewhat smaller than for the other four rather than somewhat larger.

Allantoin would be expected to have a resonance energy somewhat smaller than the sum for two urea groups and one amide group, since the amide and one urea group interfere through the sharing of NH. The experimental value, 4.7 v.e., is, however, somewhat larger than the corresponding sum $2\times1.59+0.91=4.09$ v.e.

The resonance energies of the seven purine derivatives given in Table VIII vary in an easily interpretable manner between 2.5 and 5.5 v.e. The value 2.5 v.e. for 7-methylpurine is probably a little too low, for the five-membered ring would be expected to contribute about 1.0 v.e. in addition to the 1.7 v.e. for the benzene-type six-membered ring. The introduction of an oxygen atom, with its accompanying increase in the number of possible positions for the double bond, increases the resonance energy to 3.5 v.e. for 8-oxypurine. Two oxygen atoms, in caffeine, theobromine, and xanthine, lead to an additional increase to 4.4 v.e., 4.7 v.e., and 4.9 v.e., respectively (the differences of the three values being probably without significance). Uric acid, containing three oxygen atoms, has a resonance energy of 5.2 v.e. In guanine, with one oxygen and one nitrogen atom providing extra resonance, the resonance energy is 5.5 v.e. Hence we learn

TABLE VIII. *Ureides and purines.*

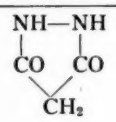
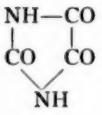
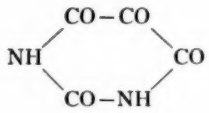
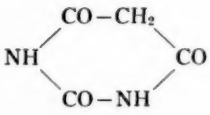
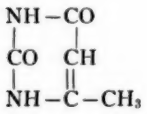
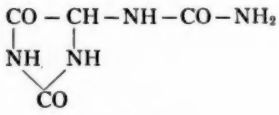
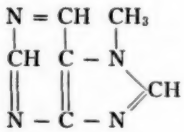
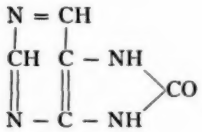
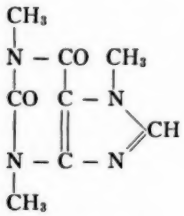
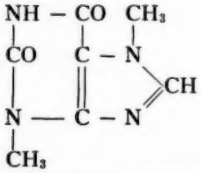
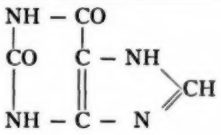
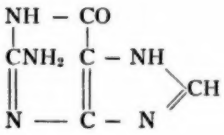
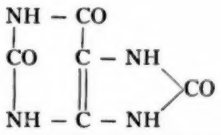
| Compound | Formula | Structure | *E* | *E'* | Resonance energy |
|---|---|---|---|---|---|
| Hydantoin | $C_3H_4N_2O_2$ |  | 49.6 | 46.5 | 3.1 |
| Parabanic Acid | $C_3H_2N_2O_3$ |  | 49.0 | 46.4 | 2.6 |
| Alloxan | $C_4H_2N_2O_4 \cdot H_2O$ |  | 70.27 | 67.95 | 2.32 |
| Barbituric Acid | $C_4H_4N_2O_3$ |  | 61.5 | 58.7 | 2.8 |
| 4-methyluracil | $C_5H_6N_2O_2$ |  | 69.0 | 66.2 | 2.8 |
| Allantoin | $C_4H_6N_4O_3$ |  | 75.9 | 71.2 | 4.7 |
| 7-methylpurine | $C_6H_6N_4$ |  | 73.6 | 71.1 | 2.5 |
| 8-oxypurine | $C_5H_4N_4O$ |  | 67.1 | 63.6 | 3.5 |
| Caffeine | $C_8H_{10}N_4O_2$ |  | 108.5 | 104.1 | 4.4 |
| Theobromine | $C_7H_8N_4O_2$ |  | 96.7 | 92.0 | 4.7 |

TABLE VIII. (*Continued*).

| | | | | | |
|---|---|---|---|---|---|
| Xanthine | $C_5H_4N_4O_2$ |  | 73.0 | 68.1 | 4.9 |
| Guanine | $C_5H_5N_5O$ |  | 75.4 | 69.9 | 5.5 |
| Uric Acid | $C_5H_4N_4O_3$ |  | 77.7 | 72.5 | 5.2 |

that each oxygen atom attached to the purine group carries with it a contribution of about 0.9 v.e. to the resonance energy of the molecule, in addition to the resonance energy included in the ketonic C=O bond energy value. The data for guanine indicate that the contribution of a nitrogen atom is still larger, though this may be due to experimental error.

It may be mentioned that in heterocyclic systems as well as in hydrocarbon condensed ring systems the contribution to the normal state of structures associated with all of the possible positions of the double bonds is dependent on the existence of a coplanar arrangement of the pertinent atoms, with bond angles of about 120°, which requires that the rings contain five or six or possibly seven atoms.

## CONCLUSION

This study of thermochemical data for a very large number of substances has shown that in every case for which the data are reliable the observed energy of the molecule is equal to that calculated for an assumed distribution of bonds or differs from it in the direction corresponding to greater stability, in accord with the quantum-mechanical requirement that the actual energy for the normal state of any system is the lower limit for values of the energy integral calculated for any wave function. For molecules for which several electronic structures make appreciable contributions to the wave function for the normal state, values of the resonance energy of 0.2 v.e. to 10 v.e. are found. Thus in benzene, pyridine, etc., the resonance energy is about 1.7 v.e. or 39,000 cal./mole, in naphthalene and quinoline about 3.1 v.e., and larger in larger condensed ring systems. In the carboxylic acids and other compounds in which a double bond resonates between two positions the energy of this resonance is about 1.2 v.e.; and in compounds such as urea, with three positions for the double bond, the resonance energy is about 1.8 v.e. Additional resonance energy is also found to accompany any increase in length of the conjugated system, as in phenylethylene, biphenyl, etc. In the preceding paper there has been given the quantum-mechanical discussion of benzene and naphthalene, and a similar treatment of open-chain conjugated systems, biphenyl, the hydroaromatic hydrocarbons and other systems will be published later.

# The Kinetics of the Thermal Decomposition of Methyl Ethyl Ether

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(Received May 31, 1933)

The kinetics of the decomposition of methyl ethyl ether have been reinvestigated. The results obtained differ considerably from those of Glass and Hinshelwood. The heat of activation is found to be 54,500±1500 calories. This value brings the activation energy of methyl ethyl ether into line with those of the other ethers.

## INTRODUCTION

HINSHELWOOD and his coworkers have investigated a series of unimolecular ether decompositions.[1] These furnish the most complete existing set of kinetic investigations involving chemically related substances. The comparison of the rates and temperature coefficients of these reactions is therefore of considerable interest.[2] If we consider the series dimethyl ether, methyl ethyl ether, diethyl ether, we have energies of activation of 58,500, 47,000, and 53,000 calories, respectively. Kassel suggests that the low value for methyl ethyl ether is due to the asymmetry of the molecule as compared with the symmetrical ethers.

In the course of another investigation[3] a few runs were made with methyl ethyl ether. These indicated that the temperature scale in the investigation of Glass and Hinshelwood was considerably in error, and that much higher temperatures were necessary for the attainment of a given rate of reaction. This conclusion is substantiated by the fact that in the investigation of Clusius[4] the rates given for the decomposition of methyl ethyl ether catalyzed by iodine are *slower* than those given by Glass and Hinshelwood for the uncatalyzed reaction.

It was therefore considered to be worth while repeating the work of Glass and Hinshelwood. The present investigation has been confined to a determination of the temperature coefficient of the reaction, inasmuch as a thorough investigation of the mechanism is being made elsewhere.[5]

## EXPERIMENTAL PROCEDURE

The reaction velocities were measured in the usual way by observing the rate of pressure change in a system at constant volume. The reaction vessel was of fused silica. The apparatus was identical with one which has been used in a number of previous investigations.[6] The required temperatures were obtained by the use of a bath of molten lead of about 6 liters capacity, which has been previously described.[7] Temperatures were measured with a chromel-alumel thermocouple in conjunction with a Cambridge thermocouple potentiometer. The temperature could be maintained constant to within 0.1°C.

Eastman's C.P. methyl ethyl ether was used. It was dried over sodium and fractionally distilled, the middle third being retained (B. P. 8–10°C).*

## EXPERIMENTAL RESULTS

As in the investigation of Glass and Hinshelwood, the reaction rates have been inferred from a comparison of the times for a given fractional pressure increase. As the reaction is by no means an ideal unimolecular one, it is desirable to use

[1] Hinshelwood, Proc. Roy. Soc. **A114**, 84 (1927); Hinshelwood and Askey, ibid. **A115**, 215 (1927); Glass and Hinshelwood, J. Chem. Soc. **1929**, 1804.

[2] See Kassel, *Kinetics of Homogeneous Gas Reactions*, New York, 1932.

[3] Steacie, J. Phys. Chem. **36**, 1562 (1932).

[4] Clusius, J. Chem. Soc. **1930**, 2607.

[5] W. Ure, private communication.

[6] Steacie, Can. J. Research **6**, 265 (1932); J. Phys. Chem. **36**, 1562 (1932).

[7] Steacie, J. Chem. Phys. **1**, 313 (1933).

* The Eastman Kodak Co. have kindly informed me of the method of preparation. The ether was prepared from sulphuric acid and a mixture of methyl and ethyl alcohols. It was therefore entirely free from iodides.

rates as near the start of the reaction as possible, and hence the times for a 25 percent increase in pressure have been used. In the absence of a detailed knowledge of the mechanism of the reaction, the amount of reaction to which this corresponds is unknown. It should, however, give a reasonably accurate criterion of the relative rates of reaction under different conditions of temperature and pressure.

The experimental observations are given in Table I.

TABLE I.

| Temperature (°C) | Initial pressure (cm) | $T_{25}$ (sec.) | Temperature (°C) | Initial pressure (cm) | $T_{25}$ (sec.) |
|---|---|---|---|---|---|
| 460 | 72.17 | 2508 | 500 | 19.20 | 536 |
| 460 | 56.76 | 2760 | 500 | 14.18 | 617 |
| 460 | 37.58 | 3222 | 500 | 11.49 | 738 |
| 460 | 25.45 | 3804 | 500 | 7.80 | 876 |
| 480 | 72.06 | 882 | 520 | 74.33 | 153.6 |
| 480 | 57.44 | 942 | 520 | 44.83 | 165.0 |
| 480 | 50.34 | 1020 | 520 | 33.84 | 189.0 |
| 480 | 31.89 | 1290 | 520 | 24.26 | 214.2 |
| 480 | 22.84 | 1464 | 520 | 17.06 | 240.0 |
| 480 | 20.06 | 1530 | 520 | 12.16 | 283.2 |
| 480 | 14.46 | 1800 | 520 | 9.32 | 317.4 |
| 480 | 11.66 | 1812 | 540 | 59.90 | 72.0 |
| 480 | 8.48 | 2124 | 540 | 35.57 | 86.4 |
| 500 | 72.13 | 328 | 540 | 23.00 | 101.4 |
| 500 | 56.88 | 341 | 540 | 14.13 | 118.8 |
| 500 | 35.91 | 438 | 540 | 9.22 | 136.8 |
| 500 | 26.05 | 490 | 560 | 65.00 | 25.8 |

The high pressure rates of reaction have been obtained by plotting $T_{25}$ against the reciprocal of the initial pressure, so as to obtain lines of slight curvature, and extrapolating to infinite pressure. The curve for 520°C is shown in Fig. 1.

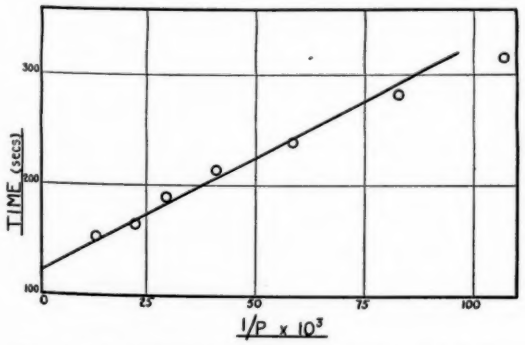


FIG. 1. Extrapolation of rates of reaction to infinite pressure.

The heat of activation has been calculated in the usual way by plotting log $T_{25}$ against $1/T$, and measuring the slope of the line. For the sake of comparison, the values of log $T_{25}$ for an initial pressure of 65 cm have been used, as well as those for infinite pressure. The data are given

TABLE II.

| Temperature (°C) | 460 | 480 | 500 | 520 | 540 | 560 |
|---|---|---|---|---|---|---|
| $T_{25}(P_0=65$ cm) | 2616 | 930 | 336 | 156.0 | 71.4 | 25.8 |
| $T_{25}(P_0=\infty)$ | 1836 | 648 | 252 | 120.0 | 55.2 | —— |

in Table II, and are plotted in Fig. 2. The values of the heat of activation thus obtained are:

| | |
|---|---|
| from $P_0=65$ cm | 55,200 cal./gram mol. |
| from $P_0=\infty$ | 53,800 cal./gram mol. |

The mean value is thus 54,500 cal., with a probable error of about 1500 calories.

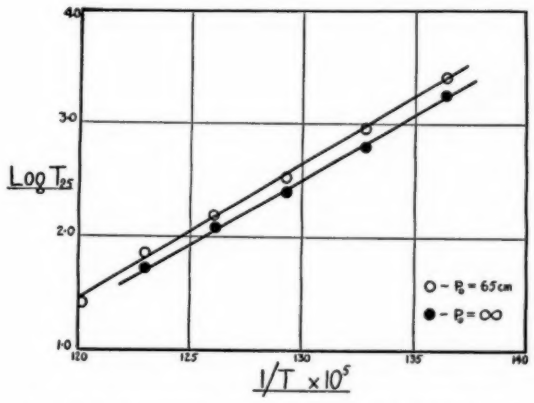


FIG. 2. The temperature coefficient of the reaction.

This is considerably higher than the value previously reported by Glass and Hinshelwood. This result gives a more regular gradation of activation energy with chemical composition for the various series of ethers which may be chosen. Thus for the series dimethyl, methyl ethyl, methyl propyl ether instead of 58,000, 47,000, 49,000 cals., we have 58,000, 54,500, 49,000. And for the series dimethyl, methyl ethyl, diethyl ether we now have 58,000, 54,500, 53,000 cal.

The main result, therefore, is to bring the heat of activation of methyl ethyl ether into line with those of the other ethers.

# The Heat Capacities and Entropies of Calcium and Barium Sulfates from 15 to 300°K. The Entropy and Free Energy of Sulfate Ion

WENDELL M. LATIMER, J. F. G. HICKS, JR., AND PHILIP W. SCHUTZ, *Chemical Laboratory, University of California*

(Received May 22, 1933)

The heat capacities of $BaSO_4$ and small precipitated crystals of $CaSO_4 \cdot 2H_2O$ have been measured from 15 to 300°K. The heat capacity of large naturally occurring gypsum crystals was measured from 60 to 274°K. The $C_p$ against log $T$ plots of the molal heat capacities of the two samples of $CaSO_4 \cdot 2H_2O$ differing in crystal surface by a factor of roughly $10^6$ show slight deviations from each other. We believe these variations to be outside the limits of experimental error. However, they do not produce a change in entropy at 298.1°K. $S°_{298.1}$ of $CaSO_4 \cdot 2H_2O$ and $BaSO_4$ were determined to be 46.36 and 31.51 E.U. respectively with an accuracy of 0.05 percent. The final value of $S°_{298.1}$ of $SO_4^{--}$ from this series of measurements is 3.5 E.U. The free energy of formation of $SO_4^{--}$ has been calculated as $-175{,}300$ cal.

THE determination of the entropies of calcium and barium sulfates enables a further check to be made on the entropy of sulfate ion in solution.[1]

## Calcium Sulfate Dihydrate

This salt was chosen in this series for two reasons: (1) the thermal data for the reaction

$$CaSO_4 \cdot 2H_2O = Ca^{++} + SO_4^{--} + 2H_2O$$

appear to be unusually good and (2) they afford a convenient medium for investigating the effect of crystal size on the entropy of solids, since large natural crystals of gypsum of high purity are easily available along with the usual precipitated material.

The heat capacity of precipitated $CaSO_4 \cdot 2H_2O$ was measured from 14 to 300°K by the experimental method of Latimer and Greensfelder.[1] Heat capacity measurements on the natural crystals were obtained from 60 to 274°K. The agreement between the two sets of results at lower temperatures precluded the necessity of extending measurements on the larger material to 14°K.

[1] For complete references to the general theory and previous work in this field, see the authors, (a) J. Am. Chem. Soc. **55**, 971 (1933); (b) J. Chem. Phys. **1**, 424 (1933).

### Material

Baker and Adamson's C.P. $CaSO_4 \cdot 2H_2O$ was intimately stirred with water and then filtered by suction. After drying, a sample of material was heated to 520°C in a muffle furnace and showed a water content of 20.85 percent as compared with the theoretical value of 20.93 percent. The sample contained no carbonate or barium and showed only a trace of sodium. The crystals were approximately $1\mu$ in length. Specific heat measurements were made on a sample weighing 67.783 grams (0.3937 moles).

The natural gypsum was obtained from a large clear single crystal (500 g) which had a water content of 20.88 percent. The size of the pieces used was limited only by the size of the calorimeter. About three-fourths of the material were pieces longer than 1 cm and no fine powder was added. Measurements were made on a sample weighing 95.630 g (0.5554 moles).

### Measurements

From 62 up to 103°K the $C_p$ of the larger crystals lies not more than 0.1 $C_p$ units below that of the smaller crystals. At 103°K the two curves cross and up to 144°K the curve for the large material falls about the same amount above that for the small material. The areas between the curves in these two regions, being very nearly equal and of opposite sign, cancel each other and therefore do not affect the entropy

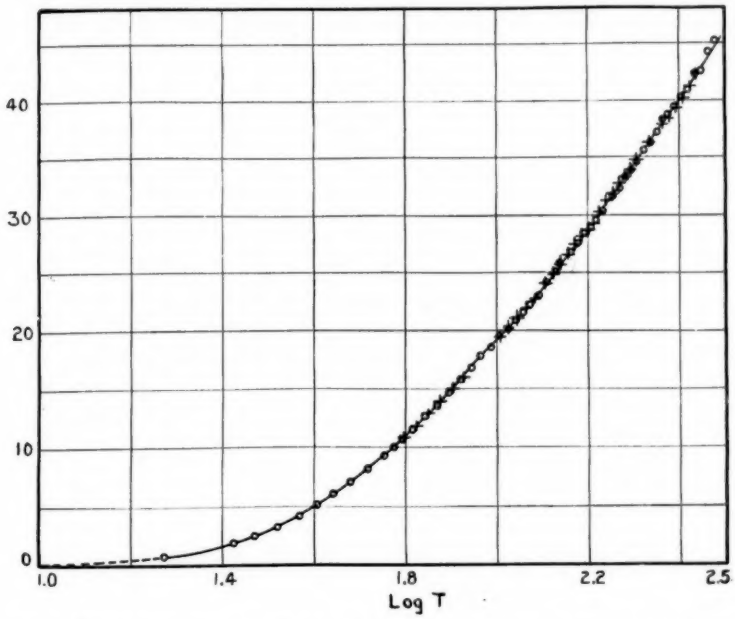


FIG. 1. Molal heat capacity of $CaSO_4 \cdot 2H_2O$. Circles, small crystals, plusses, large crystals.

of the solid at 144°K. Beginning at 144°K the $C_p$ of the large crystals again rises above that of the small ones, the deviation between the two curves reaching a maximum of 0.3 $C_p$ units at 174°K. At 206°K the curves again cross, the $C_p$ of the large crystals falling below that of the small. The maximum deviation between them is again 0.3 $C_p$ units and is reached at about 240°K. Above this temperature the two curves again approach coincidence. The areas between the curves in these last two regions cancel each other so that the entropies of the two forms agree within 0.01 E.U. This is well within the limit of error of the method. Thus, while the heat capacity curves show definite differences (on a larger scale plot than Fig. 1) for the two crystal magnitudes, the entropy of the solid material at 298.1°K is not affected. The temperature intervals employed were as follows: below 30°K about 3° per run; 30 to 200°K about 5° per run and above 200°K, about 8° per run. (See Table I.)

### Entropy of $CaSO_4 \cdot 2H_2O$

The entropy of $CaSO_4 \cdot 2H_2O$ was obtained by graphical integration of the expression

$$S°_{298.1} = \int_0^{298.1} C_p \, d \ln T$$

with a large scale curve similar to that shown in Fig. 1. The curve was extrapolated to 0°K by

TABLE I. $CaSO_4 \cdot 2H_2O$.

| $T$ | Molal $C_p$ | $T$ | Molal $C_p$ | $T$ | Molal $C_p$ | $T$ | Molal $C_p$ |
|---|---|---|---|---|---|---|---|
| | | | *Small Crystals* | | | | |
| 18.70 | 0.68 | 69.29 | 12.61 | 128.39 | 24.09 | 203.45 | 34.63 |
| 26.71 | 1.90 | 73.72 | 13.62 | 134.97 | 25.13 | 210.22 | 35.65 |
| 29.64 | 2.48 | 78.41 | 14.71 | 140.21 | 25.80 | 217.27 | 36.32 |
| 33.18 | 3.20 | 83.24 | 15.79 | 145.36 | 26.68 | 224.91 | 37.20 |
| 37.11 | 4.21 | 88.04 | 16.83 | 150.72 | 27.51 | 231.90 | 38.33 |
| 40.36 | 5.15 | 92.37 | 17.81 | 155.86 | 28.41 | 238.23 | 38.79 |
| 43.77 | 5.99 | 96.80 | 18.58 | 160.80 | 28.92 | 245.64 | 39.54 |
| 47.84 | 6.98 | 101.26 | 19.47 | 165.73 | 29.61 | 254.02 | 40.36 |
| 51.98 | 8.19 | 105.59 | 20.15 | 170.86 | 30.36 | 263.29 | 41.01 |
| 56.56 | 9.33 | 109.84 | 20.85 | 179.79 | 31.68 | 272.18 | 42.30 |
| 59.47 | 10.03 | 114.04 | 21.52 | 185.78 | 32.34 | 282.11 | 42.63 |
| 62.00 | 10.73 | 118.22 | 22.25 | 191.39 | 33.25 | 292.67 | 44.29 |
| 65.34 | 11.54 | 123.62 | 22.95 | 197.61 | 33.93 | 302.10 | 45.17 |
| | | | *Large Crystals* | | | | |
| 62.40 | 10.79 | 115.89 | 21.95 | 158.83 | 28.84 | 203.57 | 34.83 |
| 66.74 | 11.85 | 120.88 | 22.75 | 162.93 | 29.50 | 216.12 | 36.35 |
| 70.84 | 12.91 | 127.59 | 23.97 | 168.21 | 30.30 | 231.29 | 37.93 |
| 75.20 | 13.92 | 133.12 | 24.85 | 173.77 | 31.28 | 239.57 | 38.38 |
| 80.05 | 14.99 | 138.32 | 25.70 | 179.48 | 31.89 | 247.81 | 39.37 |
| 84.70 | 16.02 | 143.42 | 26.48 | 185.26 | 32.71 | 256.44 | 40.23 |
| 101.38 | 19.42 | 148.83 | 27.35 | 190.98 | 33.28 | 265.23 | 41.34 |
| 105.96 | 20.34 | 153.84 | 28.15 | 196.78 | 34.05 | 274.13 | 42.25 |
| 110.77 | 21.18 | | | | | | |

means of the Debye $T^3$ rule, $\theta = 167.2$. A summary of the entropy calculation is given in Table II.

TABLE II.

| | | |
|---|---|---|
| 0–19.95°K | Extrapolation | 0.263 E.U. |
| 19.95–298.1°K | Graphical | 46.097 E.U. |
| Entropy at 298.1 of $CaSO_4 \cdot 2H_2O$ = 46.36 E.U. ±0.05 percent | | |

**Heat of solution**

Lange and Monheim[2] give 273±20 calories per mole as the heat of solution of $CaSO_4 \cdot 2H_2O$ at infinite dilution and 298.1°K. This value has been used in the present calculation. We have then:

$$CaSO_4 \cdot 2H_2O(s) = CaSO_4 \cdot 2H_2O(aq)\ \Delta H = 273 \text{ cal.}$$

**Free energy of solution**

Lange and Monheim[2] give the solubility of $CaSO_4 \cdot 2H_2O$ as 0.0156 mole per 1000 grams of water, which agrees well with that given by Fosbinder.[3]

The activity coefficient of $CaSO_4 \cdot 2H_2O$ in a saturated solution is given by Fosbinder[3] as 0.312. The free energy of solution is

$$\Delta F^\circ_{298.1} = -1363.8 \log [(0.0156)(0.312)]^2 = 6308 \text{ calories.}$$

**Entropy of sulfate ion**

Substituting the above values in the equation, $\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T$, we obtain for the reaction $CaSO_4 \cdot 2H_2O(s) = Ca^{++} + SO_4^{--} + 2H_2O$ (hypothetical one molal solution) $\Delta S^\circ_{298.1} = -20.2$ E.U. Using the values $S^\circ_{298.1}$ of $Ca^{++} = -11.4$,[1] $S^\circ_{298.1}$ of $H_2O = 16.9$[4] and applying the third law, we obtain:

$$-20.2 = S^\circ_{298.1}SO_4^{--} - 11.4 + 33.8 - 46.4;$$
$$S^\circ_{298.1}SO_4^{--} = 3.8 \text{ E.U.}$$

## BARIUM SULFATE

The heat capacity of $BaSO_4$ was measured from 15 to 300°K by the same experimental method as before.[1] Muller's[5] data on the heat of solution and Neuman's[6] data on the solubility and activity coefficient of barium sulfate were used to calculate the entropy change involved in the transfer of one mole of barium sulfate from the solid state to an hypothetical one molal solution. The entropy of $Ba^{++}$ was recalculated from the data of Latimer and Ahlberg[1] on barium and thallous nitrates. A survey of the existing data on the thallous halides gives 28.6 E.U. as the most consistent value for the standard entropy of $Tl^+$. This is the same value as that employed by Latimer and Ahlberg. Using 28.6 E.U. gives as the standard entropy of $NO_3^-$ a value of 36.9 E.U. This figure yields 0.8 E.U. for the entropy of $Ba^{++}$ in its standard state.

**Material**

Barium sulfate of C.P. quality was recrystallized twice from concentrated sulfuric acid. The salt was washed repeatedly with hot distilled water to remove excess acid. After the washing it was found necessary to ignite the salt to constant weight in order to remove the last traces of acid. Specific heat measurements were carried out on a sample weighing 83.043 g (0.78290 mol.) All weights were reduced to vacuum standard.

**Measurements**

The molal heat capacity values fall on a smooth curve which exhibits several points of double inflection. At the higher temperatures the points deviate somewhat. This is because of large radiation corrections necessary at these temperatures, and to the possible presence of water vapor in the apparatus. The experimental results are presented in Table III and graphically as a

TABLE III. *$BaSO_4$*.

| $T$ | Molal $C_p$ | $T$ | Molal $C_p$ | $T$ | Molal $C_p$ | $T$ | Molal $C_p$ |
|---|---|---|---|---|---|---|---|
| 15.72 | 0.75 | 65.96 | 9.91 | 124.84 | 15.68 | 201.87 | 20.12 |
| 18.62 | 0.93 | 69.61 | 10.39 | 130.19 | 16.03 | 210.18 | 20.65 |
| 21.49 | 1.40 | 73.63 | 10.94 | 135.48 | 16.37 | 218.44 | 20.98 |
| 24.42 | 1.86 | 77.79 | 11.47 | 140.83 | 16.71 | 228.03 | 21.57 |
| 26.83 | 2.36 | 81.73 | 11.84 | 146.18 | 17.00 | 237.28 | 21.82 |
| 30.56 | 3.19 | 85.52 | 12.34 | 151.76 | 17.41 | 246.86 | 21.92 |
| 34.94 | 4.04 | 89.65 | 12.85 | 158.06 | 17.77 | 256.21 | 22.60 |
| 39.83 | 5.13 | 94.22 | 13.31 | 164.59 | 18.17 | 267.62 | 23.47 |
| 44.75 | 6.13 | 104.17 | 14.11 | 171.16 | 18.51 | 277.68 | 23.71 |
| 49.69 | 7.10 | 109.29 | 14.52 | 178.13 | 18.89 | 288.69 | 24.30 |
| 54.95 | 8.04 | 114.25 | 14.92 | 185.78 | 19.36 | 298.23 | 24.14 |
| 60.49 | 8.99 | 119.44 | 15.27 | 193.94 | 19.81 | | |

[2] Lange and Monheim, Zeits. f. physik. Chemie **A150**, 349 (1930).

[3] Fosbinder, J. Am. Chem. Soc. **51**, 1345 (1929).

[4] Giauque and Ashley, Phys. Rev. **43**, 1 (1933).

[5] Muller, Bull. Soc. Chim. **23**, 13 (1918).

[6] Neuman, J. Am. Chem. Soc. **55**, 879 (1933).

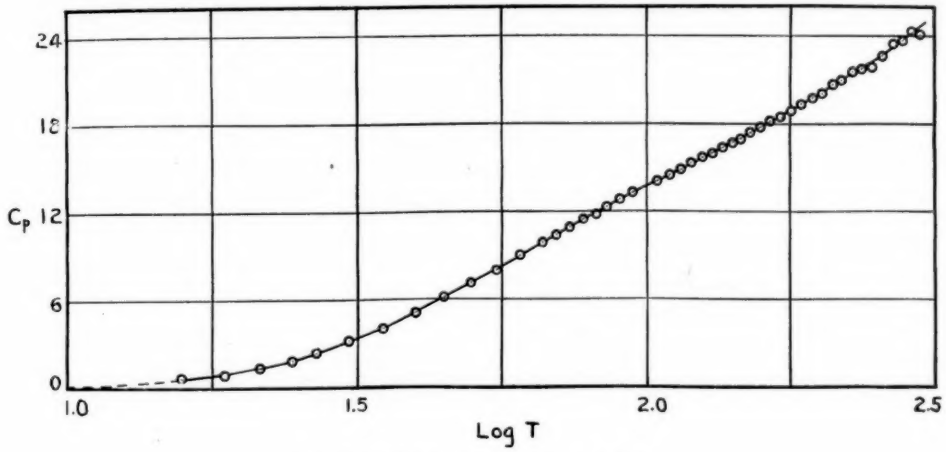


FIG. 2. Molal heat capacity of $BaSO_4$.

function of log $T$ in Fig. 2. The heating intervals employed in various temperature regions were the same as with calcium sulfate.

### Entropy of barium sulfate

The entropy of $BaSO_4$ was obtained by graphical integration of the expression

$$S_{298.1}=\int_0^{298.1} C_p d \ln T$$

from the curve shown in Fig. 2. The curve was extrapolated below 15°K by means of the Debye $T^3$ rule, $\theta=148.4$. A summary of the entropy calculation is given in Table IV.

TABLE IV.

| | |
|---|---|
| 0–20°K Integration of $T^3$ expression | 0.379 E.U. |
| 20–298.1°K Graphical | 31.134 E.U. |
| Entropy at 298.1°K of $BaSO_4$ = 31.51 ± 0.05 percent | |

### Heat and free energy of solution

Muller[5] gives $\Delta H^\circ_{298.1}$ of solution as 5455 cal. Neuman's[6] data yield $\Delta F^\circ_{298.1}$ of solution equal to 13,718 from the equation $\Delta F^\circ_{298.1}=-1363.8 \log (\gamma m)^2$, where $\gamma=0.977$ and $m=0.957\times10^{-5}$ $m/1$.

### Entropy of solution

Substituting the above values in the equation $\Delta S^\circ=(\Delta H^\circ-\Delta F^\circ)/T$, we have for the reaction $BaSO_4(s)=Ba^{++}+SO_4^{--}$ (hypothetical one molal solution); $\Delta S^\circ_{298.1}=-27.7$ E.U. Application of the third law yields

$$-27.7=0.8+S^\circ_{SO_4^{--}}-31.5;\ S^\circ_{SO_4^{--}}=3.0 \text{ E.U.}$$

### Summary of values for the entropy of sulfate ion

From the three separate determinations, i.e., from silver sulfate, calcium sulfate and barium sulfate, we find the entropy of sulfate ion to be 2.8, 3.8 and 3.0 E.U., respectively. The agreement is good considering the difficulties of obtaining accurate values for the entropies of solution. The solution entropy appears to be much more reliable for the calcium sulfate and we believe the entropy, 3.8 E.U. obtained from the measurements on this salt to be accurate to 0.5 E.U. Giving some weight to the other values, however, we have chosen 3.5 as the best value for the entropy of sulfate ion ($S^\circ_{H^+}=0$) in hypothetical 1 molal solution.

### The free energy of sulfate ion

The heat of formation of sulfuric acid is rather accurately known. Roth, Graw and Meischner[7] give for the reaction

$$S_{rh}+H_2(g)+2O_2(g)=H_2SO_4(1)$$

$$\Delta H^\circ_{298.1}=-194{,}150\pm100 \text{ cal.}$$

Correcting this to 298.1°K we have

$$\Delta H^\circ_{298.1}=-194{,}120\pm100 \text{ cal.}$$

Extrapolation of the heat of dilution data of

[7] Roth, Graw and Meischner, Zeits. f. anorg. Chemie **193**, 161 (1930).

Graw and Roth[8] and Brönsted[9] to infinite dilution gives

$$H_2SO_4(1) = H_2SO_4(aq) \quad \Delta H = -20{,}900 \text{ cal.}$$

Combining these, we have

$$H_2(g) + S(rh) + 2O_2(g) = H_2SO_4(aq)$$
$$\Delta H^\circ_{298.1} = -215{,}000 \text{ cal.}$$

Then using the entropies $S^\circ_{298.1}$ of $H_2 = 31.23$, $S^\circ_{298.1}$ of $S = 7.6$, $S^\circ_{298.1}$ of $O_2 = 49.03$, $S^\circ_{298.1}$ of $SO_4^{--} = 3.8$, $\Delta S^\circ_{298.1}$ for the above reaction is $-133$ E.U.

Substituting these values in the equation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$, we calculate for the free energy of formation of aqueous sulfuric acid, $\Delta F^\circ_{298.1} = -175{,}300$ cal. This value is just outside the limits of error ($\pm 1000$ cal.) set by Lewis and Randall[10] on Bichowsky's value of 176,500 calories.

The authors extend their thanks to Sally R. Hicks for her assistance with the calculations.

[8] Graw and Roth, Zeits. f. anorg. Chemie **188**, 184 (1930).

[9] Brönsted, Zeits. f. physik. Chemie **68**, 693 (1910).

[10] Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw Hill Book Company, New York, 1923.

# LETTERS TO THE EDITOR

*This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.*

## A Remark on Rosen's Paper: "Lifetimes of Unstable Molecules"

In a recent number of this journal, Rosen[1] has made an interesting calculation on the lifetimes of unstable molecules. He supposes that there are three atoms in a line, the two outside atoms each being connected to the inside atom by a potential of the Morse type; we thus have two vibrators which interact because they have one atom in common. Assuming then that one of the vibrators is in a relatively low, but not the lowest vibrational state, and that the energy of the other is near the dissociation level, he calculates the probability of dissociation, and hence the lifetime of the molecule, by a perturbation method. In making this calculation he considers a special case. The vibrator in a relatively low state, with vibrational quantum number $m$, is supposed to drop back to the lowest state (vibrational quantum number zero), the energy being taken up in the transition into the continuum representing dissociation of the other vibrator. Then, in the particular case Rosen considers, if $m=1$ the lifetime of the unstable triatomic molecule is of the order of $2^{-1}\times10^{-14}$ seconds, while if $m$ is greater than 1 the lifetime is much greater; for $m>4$ the lifetime is very large compared to the time between collisions at moderate pressures. Rosen therefore concludes that if $m>4$ there is very little chance of the molecule decomposing before it exchanges energy at a collision.

There is, however, another factor which comes into this problem, which is not considered in Rosen's paper. It is, indeed, true that the probability of a transition *directly* into the continuum decreases very greatly as $m$ increases, or, in general, as the amount of energy which is transferred from the one vibrator to the other increases. But it is not necessary that the exchange of energy should take place in one step; it can take place through a series of exchanges of smaller amounts of energy between the vibrators without dissociation taking place, until one of them is in a state where its probability of dissociation is great. It is obvious that the probability of dissociation ultimately taking place will then not fall off so rapidly as $m$ increases. Even when only discrete states are involved, it is not necessary to have any exact matching of the unperturbed energy levels; for the lifetime obtained by Rosen when $m=1$, namely, $2^{-1}\times10^{-14}$ seconds, which is of the order of the inverse frequency of molecular vibrations, indicates a sufficiently large perturbation so that this is not necessary. Of course in order to be absolutely sure of this point, one really ought to calculate out matrix components for transitions which involve exchanges of energy without dissociation, and this will be done in work which Mr. Harold Gershinowitz is starting; in the meantime, however, we may consider it to be pretty certain that these matrix components will be large enough so that the above statement will be true. We should perhaps add that the whole picture becomes very crude when these matrix components are large; but the present statement is sufficiently good for the purposes of this note.

From Rosen's calculation one may probably infer that in general in a complex molecule it is very unlikely that a direct transition to a dissociated state will occur unless an amount of energy nearly sufficient for dissociation is already present in the vibrator which is going to break. This agrees with the assumption made by Rice and Ramsperger and by Kassel[2] and later discussed in some detail by various writers[3] that such a molecule will decompose only if sufficient energy is localized in a particular place in the molecule. Rosen's calculation might at first

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[1] Rosen, J. Chem. Phys. **1**, 319 (1933).

[2] Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927); Kassel, J. Phys. Chem. **32**, 225, 1065 (1928); see also Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).

[3] Rice, *Réunion Internationale de Chimie Physique*, p. 298, Paris, 1928; Kassel, *Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co.; Eyring, Chem. Rev. **10**, 111 (1932); Evans, Trans. Far. Soc. **28**, 840 (1932).

sight have been thought to be in conflict with the theories of Rice and Ramsperger and of Kassel, since it does not appear to provide the mechanism by which the energy can become localized, but the considerations here presented seem to indicate that it is in very good accord with these theories and that it brings out the factors involved in an interesting manner.

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July, 1933.

## The Calculation of Matrix Elements Between Bond Eigenfunctions

In a recent paper in this journal[1] we described a method of calculating the matrix elements between bond eigenfunctions. In the same issue Pauling[2] described another method of obtaining the same results. Although Pauling's method of obtaining these matrix elements is faster than the process we described in the paper referred to above, a modification of our method has been found to be equal to Pauling's in speed, and does not require the construction of Pauling's bond superposition patterns.

The coefficient of the coulombic integral $C$ is obtained in the same manner as before. The diagram of spin assignments, to take the same example, is

$$\begin{array}{cccccccc} \alpha & \beta & \beta & \alpha & \alpha & \beta & \beta & \alpha \\ a-b & & c-d & & e-f & & g-h & \end{array}$$

$$\begin{array}{cccccccc} & a-c & & b-d & & e-g & & f-h \\ \alpha & \beta & \beta & \alpha & \alpha & \beta & \beta & \alpha. \end{array}$$

In the construction of this diagram the assignment of a definite spin to atom $a$ fixes the spins of $b$, $c$ and $d$. These four atoms therefore form a cycle, corresponding to an "island" in Pauling's bond superposition pattern. The atoms $e$, $f$, $g$ and $h$ also form a cycle. It is often convenient to enclose the atoms of a cycle in a curve.

We may divide the interchange integrals into three classes:

I. The two atoms lie in different cycles.

II. The two atoms lie in the same cycle and have the same spin assignment.

III. The two atoms lie in the same cycle and have opposite spin assignments.

The coefficients of all the interchange integrals in each class are the same. If $x$ is the coefficient of $C$, the coefficients of the three classes are: Class I, $-\frac{1}{2}x$; Class II, $x$; Class III, $-2x$. The proof of these statements follows immediately from our previous paper. The discussion of the integral $(ae)$ is typical of any integral of Class I; that of $(ad)$ is typical of Class II; and that of $(ab)$ is typical of Class III. The proof could equally well have been taken from Pauling's paper. In certain special cases this work can be made even shorter.

We would also like to call attention to an error in Table IV of our previous paper. The coefficient of $C$ in $H_{14,14}$ should be 5/2 instead of 5/4.

HENRY EYRING
GEORGE E. KIMBALL

Frick Chemical Laboratory,
Princeton University,
June 29, 1933.

[1] Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933).
[2] Pauling, J. Chem. Phys. **1**, 280 (1933).